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ALKALINE EARTH HALOPHOSPHATES AND RELATED PHOSPHORS[1]

H. G. JENKINS, A. H. McKEAG, AND P. W. RANBY

Communication from the Staff of the Laboratory of The General Electric Company, Limited, Wembley, England

ABSTRACT

A class of new phosphors of great technical importance is described, which enables white light to be obtained in fluorescent lamps from a single chemical compound. The new materials are alkaline earth halophosphates activated with antimony and manganese.

Luminescent properties are discussed as a function of composition and several possible substitutions. The latter include substitution of strontium or barium for calcium, of chlorine or hydroxyl ion for fluorine, of several primary activators in place of antimony, and of other activators in place of manganese in hydroxyapatites. A short account of the structure of the phosphors is presented. The mechanism of luminescence in these phosphors and some of their performance characteristics are discussed briefly.

INTRODUCTION

The alkaline earth halophosphates are a new class of luminescent materials discovered in 1942 by McKeag and Ranby (1), at the Research Laboratories of The General Electric Company in England. These phosphors, which are of the double activator type, are strongly excited by the low pressure mercury vapor discharge and are now finding widespread use in fluorescent lamps in England, where they have largely replaced zinc beryllium silicate and magnesium tungstate.

A unique feature of the halophosphates is that, while some members emit highly colored fluorescent light, the emission of others is characterized by broad spectral energy distributions which enable white light suitable for general lighting purposes to be obtained without the use of the usual blend of phosphors of widely differing luminescent and physical characteristics. The new phosphors have a matrix of apatite-like structure and the activators used are antimony and manganese. They are interesting examples of double activation: antimony alone produces strong blue luminescence similar in spectral composition to that of magnesium tungstate; manganese alone produces no photoluminescence, but in the presence of antimony it gives rise to a range of colors from pale blue to orange-red according to the amount present and the composition of the matrix.

Various other activators, such as arsenic, tin, lead, and bismuth, in place of antimony have been investigated and produce photoluminescence which can be modified by manganese (2); a number of more recently discovered related phosphors of similar structure in which the halogen is replaced by an oxy- or hydroxyl group, have also been investigated (3). The photoluminescence of these materials differs to a remarkable extent from that of the halophosphates. For example, copper, an inhibitor of luminescence

[1] Manuscript received February 28, 1949. This paper prepared for delivery before the Philadelphia Meeting, May 4 to 7, 1949.

in the latter compounds, is an efficient activator in the hydroxyphosphates.

The methods of preparation and general chemistry of these complex phosphors are discussed and an account is given of their chief luminous and other characteristics, including some observations on the structure of the matrix and positions and functions of the activators in the lattice.

PREPARATION

General.—The halophosphates discussed in the present paper can be represented by the general formula $3M_3(PO_4)_2 \cdot MX_2$ where M is one of the alkaline earth metals, calcium, strontium, or barium, or a mixture of two or more of these, and X is a halogen atom or a mixture of halogen atoms. The hydroxyphosphates are of similar composition, but with the halogen replaced by a hydroxyl group. It is proposed to discuss the main points

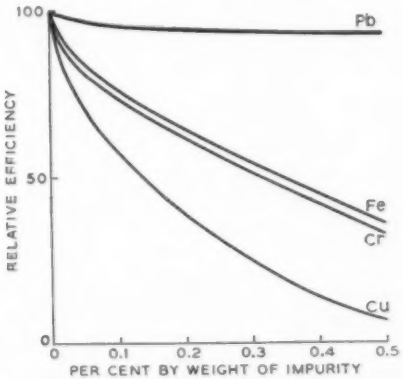

FIG. 1. Effect of impurities on the efficiency of a typical halophosphate

concerned with the preparation of only one or two of the more important members of these extensive families, namely, calcium fluo-phosphate and calcium fluo-chloro-phosphates activated by antimony and manganese. The preparation of other members of the halophosphate class follows similar lines.

In common with other inorganic phosphors, high purity of the starting materials is essential for best results, although the halophosphates appear to be markedly less sensitive than either zinc beryllium silicate or magnesium tungstate to most of the common impurities. Fig. 1 shows the effect of various deliberately added impurities on the efficiency of a typical halophosphate. Each impurity was incorporated in the mixture before firing.

It is possible to form calcium fluo-phosphate by mixing together phosphoric acid, calcium carbonate, and calcium fluoride. There is evidence to show that the fluo-phosphate is formed in this reaction without heating whereas the chlorophosphate formation appears to require subsequent heating to at least 600 C as shown by x-ray evidence. This process has given

excellent results, but because of the complexity of the reaction and its dependence on factors such as temperature, particle size, etc., it is difficult to control in practice. For this reason, it is more satisfactory to prepare components which, after mixing, combine to give the required halophosphate during the firing. This method of preparation is dealt with below.

Starting material.—Calcium halophosphates $3Ca_3(PO_4)_2 \cdot Ca(F, Cl)_2$ can be prepared by heating a mixture of calcium oxide, phosphorus pentoxide, and calcium halides in the required molecular proportions. Since, however, both calcium oxide and phosphorus pentoxide are difficult to handle, they are, in practice, replaced by other calcium and phosphorus compounds which decompose into the oxides on heating. Thus, instead of calcium oxide, it is preferable to use the carbonate, hydroxide, or even nitrate, and instead of phosphorus pentoxide, an ammonium phosphate such as $(NH_4)_2$ HPO_4 may be used. The activators, antimony and manganese, can be introduced by reheating the halophosphates with antimony trioxide and manganese carbonate in the correct proportion. It has been found desirable to separate the two thermal operations, because the evolution of reducing gases from the matrix-forming materials during the initial firing tends to reduce the antimony compound with consequent harmful effects on the resulting phosphor.

Attempts to prepare halophosphates, by precipitating calcium orthophosphate and heating this with calcium halides, have not given consistent results. This is, perhaps, not surprising since the formation of calcium ortho-phosphate by precipitation methods is extremely uncertain. The composition of the precipitate varies very considerably and depends more on the mode of precipitation than on the amounts of reactants used (4). The product is also affected by such factors as temperature during precipitation and subsequent washing and drying treatments (5). Several workers (4, 6) have shown the great variety of compositions associated with the name "Commercial calcium ortho-phosphate." Secondary calcium phosphates obtained by precipitation are much more constant. X-ray examination of the precipitate obtained from aqueous molar solutions of calcium chloride and diammonium hydrogen phosphate has shown that it consists of secondary calcium hydrogen phosphate, $Ca\ HPO_4 \cdot 2H_2O$, when precipitated cold and $CaHPO_4$ when precipitated from boiling solutions.

Heat treatment and incorporation of the activators.—Heating appropriate amounts of calcium hydrogen phosphate, calcium carbonate, calcium halide, and suitable compounds of the activating metals forms the halophosphate. Both gas and electrically heated furnaces have given good results and the firing may be carried out in closed trays, tubes, or crucibles at a temperature in the neighborhood of 1150 C, the time depending on the quantity being fired. A reducing atmosphere should be avoided during firing and care must be taken to reduce loss of halide, particularly chloride, to a minimum.

The color of the fluorescence is not greatly dependent on the concentration of antimony originally present in the unfired mixture, provided it lies between about 0.25 and 10 per cent by weight of the mixture. The efficiency of the final product is, however, dependent on the antimony content, as shown in Fig. 2. In practice, about 3 per cent of antimony introduced as the oxide or phosphate may be used, but owing to the volatility of antimony compounds at high temperatures, only about half this amount remains in the final product.

It is noteworthy that antimony can be introduced into the preformed halophosphate at temperatures greater than about 800 C. The curve in Fig. 3 shows the effect of introducing antimony to preformed material at different temperatures. Because of the marked effect of manganese on the fluorescent color, it is difficult to achieve a uniform fluorescent product by adding the manganese to well crystallized halophosphate. The best results appear to be achieved by adding both activators before firing.

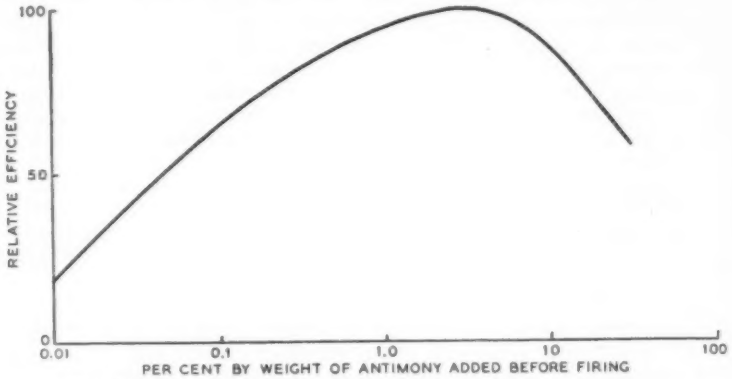

FIG. 2. Effect of added antimony on efficiency of halophosphate

TABLE I. *Fluorescent colors of calcium halophosphates excited by 2537 Å radiation*

Composition of matrix	Color of fluorescence when matrix is activated by 3% Sb and the following percentages of Mn				
	0	½	1	2	3
$3Ca_3(PO_4)_2{\cdot}1CaF_2$	Pale blue	Bluish white	Yellowish white	Pale yellow	Yellow
$3Ca_3(PO_4)_2{\cdot}\frac{1}{2}CaF_2{\cdot}\frac{1}{2}CaCl_2$	Pale blue	Whitish	Cream white	Yellow orange	Orange
$3Ca_3(PO_4)_2{\cdot}\frac{1}{2}CaF_2{\cdot}\frac{1}{2}CaCl_2$	Pale blue	Whitish	Cream white	Pale orange	Orange
$3Ca_3(PO_4)_2{\cdot}\frac{1}{2}CaF_2{\cdot}\frac{1}{2}CaCl_2$	Pale blue	Whitish	Pinkish white	Orange	Pink-red
$3Ca_3(PO_4)_2{\cdot}1CaCl_2$	Green blue	Whitish	Pinkish white	Pink	Pink-red
$3Ca_3(PO_4)_2{\cdot}\frac{1}{2}CaCl_2{\cdot}\frac{1}{2}CaBr_2$	Blue		Pink	Pink-red	Reddish

COMPOSITION AND LUMINESCENT PROPERTIES

Calcium halophosphate.—Table I shows how the fluorescent color changes with varying matrix composition and amount of manganese for a fixed amount of antimony. It will be noted that under a given set of conditions the color of the luminescence tends toward longer wavelengths with increasing atomic weight of the halogen used. The iodo compounds are, as might be expected, unstable at the formation temperature of the phosphor and useful phosphors have not yet been prepared with this halogen.

Strontium and barium halophosphates.—Calcium atoms in calcium halophosphate can be replaced partially or wholly by strontium, or even barium, atoms. The change in luminescent color of these compounds, with changing composition, follows the same general rules as the calcium compounds.

Table II shows the relationship between composition and manganese content for a group of typical strontium halophosphates. Corresponding barium compounds have also been prepared.

Substitution of other activators for antimony.—In the phosphors so far discussed, antimony is an essential constituent for producing luminescence under short ultraviolet radiation. The antimony may, therefore, be called a "sensitizing" or "primary" activator and the manganese a "modifying" or "secondary" activator.[2] The effect of the primary activator is to introduce into the halophosphate a powerful ultraviolet absorption band in the region of 2537 Å. Other elements such as arsenic, bismuth, tin, and lead can be used in place of antimony (2) and function as primary activators, but no substitute for manganese as a secondary activator has yet been

TABLE II. *Fluorescent colors of strontium halophosphates excited by 2537 Å radiation*

Composition of matrix	Color of fluorescence when matrix is activated by 3% Sb and the following percentages of Mn				
	0	½	1	2	5
$3Sr_3(PO_4)_2{\cdot}1SrF_2$	Pale blue	Blue white	Yellow white	Yellow	Deep yellow
$3Sr_3(PO_4)_2{\cdot}\frac{1}{2}SrF_2{\cdot}\frac{1}{2}SrCl_2$	Blue	Whitish	Pale pink	Orange	Deep orange
$3Sr_3(PO_4)_2{\cdot}1SrCl_2$	Blue	Blue white	Pale pink	Pink	Pink

TABLE III. *Calcium fluophosphate containing other primary activators in place of antimony*

Matrix	Activator	Color of fluorescence excited by short ultraviolet (2537 Å.)
$3Ca_3(PO_4)_2{\cdot}1CaF_2$	3% As	Blue
$3Ca_3(PO_4)_2{\cdot}1CaF_2$	4% Sn	Blue
$3Ca_3(PO_4)_2{\cdot}1CaF_2$	5% Pb	Weak blue
$3Ca_3(PO_4)_2{\cdot}1CaF_2$	7½% Bi	Yellow

found. The fluorescent colors shown by calcium fluophosphate containing these other primary activators are shown in Table III. With any of these activators, the color of the luminescence moves toward longer wavelengths with increasing amounts of manganese.

HYDROXYPHOSPHATES

The fluorescent color changes from blue to warmer colors produced by adding manganese to an antimony-activated halophosphate can be reversed by heating the halophosphate in steam. This change in color appears to be due to the gradual replacement of halogen ions by hydroxyl- or oxy-groups. For convenience, the resultant compound will be referred to in what follows as a hydroxyphosphate, although it may be wholly or in part oxyphosphate. Manganese plays no part in the blue fluorescing hydroxyphosphate which can be prepared with antimony as the sole activator by a process similar to that described above for halophosphate, except

[2] Some writers use the terms primary and secondary in the reverse sense to that employed here. See, for example, Fonda and Studer, *J. Optical Soc. Am.*, **38**, No. 12, p. 1007 (1948).

that the alkaline earth metal hydroxide is used in place of the halide in the initial mixture and the heat treatment is conducted in an atmosphere of steam.

In addition to antimony, the hydroxyphosphates can be activated by a small amount of copper—about 0.1 per cent by weight—the resulting material showing a deeper blue fluorescence than when antimony is used. This is in contrast to the halophosphates in which copper behaves as an inhibitor or "killer" of luminescence; thallium gives a characteristic blue violet fluorescence. It is somewhat surprising that manganese as a secondary activator introduces a red band into the emission, with either copper or thallium present as the primary activator, in view of its apparent inertness in the same lattice with antimony present. Similar results are obtained with strontium and barium hydroxyphosphates.

GENERAL CHARACTERISTICS

Structure.—The first technically important phosphor of the halophosphate type to be described was cadmium chlorophosphate activated by manganese, which was discovered by McKeag and Randall (7) in 1937. X-ray and chemical evidence revealed a structure for this phosphor analogous to that of apatite. The compound, which can be represented by the formula $3Cd_3(PO_4)_2 \cdot CdCl_2$, differs in several important respects from the alkaline earth halophosphates; for example, it is not activated to any significant extent by antimony, but is strongly activated by manganese giving an orange yellow fluorescence which is unaffected by the amount of manganese present over a wide range.

The new phosphors described in the present paper have also been shown by x-ray methods to possess the characteristic apatite structure (1). As already mentioned, the halophosphates can be represented by the general formula $3M_3(PO_4)_2 \cdot MX_2$, where M is an alkaline earth metal or two or more such metals and X is a halogen atom or a mixture of halogen atoms. Fig. 4 shows x-ray diffraction patterns of a number of halophosphates. These show that while replacement of fluorine by chlorine gives rise to an expansion of the lattice, the introduction of manganese causes a reduction in the dimensions of the structure cell. A consideration of the relative sizes of the respective ions shows that this is consistent with the replacement of calcium by manganese.

The effect of the introduction of the optimum amount of antimony on the lattice dimensions is extremely small, and gives no indication as to the probable positions occupied by antimony atoms in the structure. The replacement of calcium by antimony should produce a reduction in the volume of the structure cell, while the replacement of phosphorus might be expected to result in a slight increase. The very small changes in lattice dimensions which are observed could be explained if both substitutions occurred, a possibility which cannot be ignored in view of the marked basic and acidic properties possessed by antimony.

X-ray examination of the hydroxyphosphates activated by copper has shown that these are very similar in structure to the halophosphates. The problem of distinguishing between the hydroxy- and oxy-apatite forms by x-ray methods is one of some difficulty. The methods of preparation, using an atmosphere of steam, and the fact that prolonged heating

of the finished phosphor in air causes a loss of weight and a reduction of luminescence, suggest that these phosphors are of hydroxy- rather than oxy-phosphate composition.

Mechanism of luminescence.—The mechanism by which antimony enables the manganese atoms in halophosphates to emit photoluminescence is quite obscure. Rothschild (8), Schulman *et al.* (9), and Froelich (10)

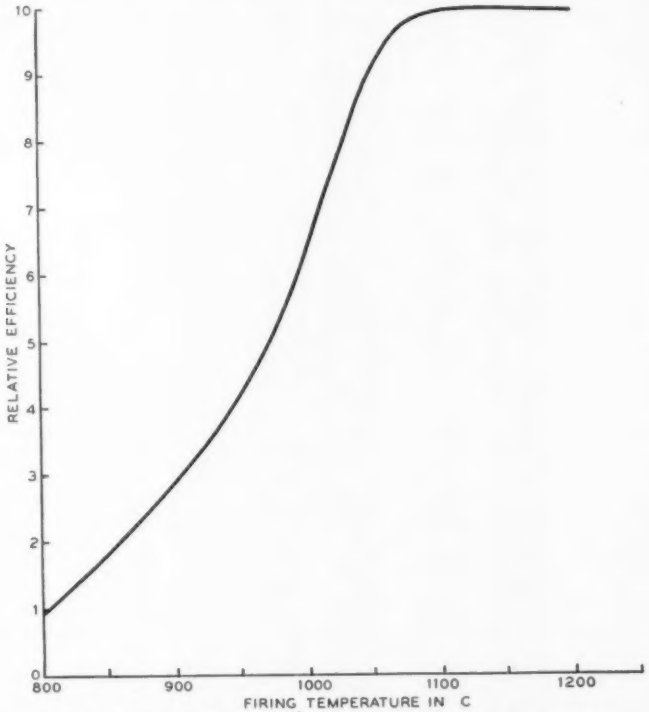

FIG. 3. Effect of firing temperature on the incorporation of antimony in preformed halophosphate.

have discussed the problem in relation to other double activated phosphors and have mentioned various ways in which the energy transfer to the manganese atoms might take place. Rothschild, for example, assumes that the ultraviolet energy absorbed by the primary activator is transferred to the secondary activator atoms by an inelastic collision process, presumably in a manner analogous to that of the sensitized excitation of thallium vapor by 2537 Å resonance radiation in the presence of mercury atoms. He refers to the emission of the secondary activator as sensitized luminescence. Froelich prefers the term double activation, since, in true sensitization, the sensitizer should not introduce an emission band of its own.

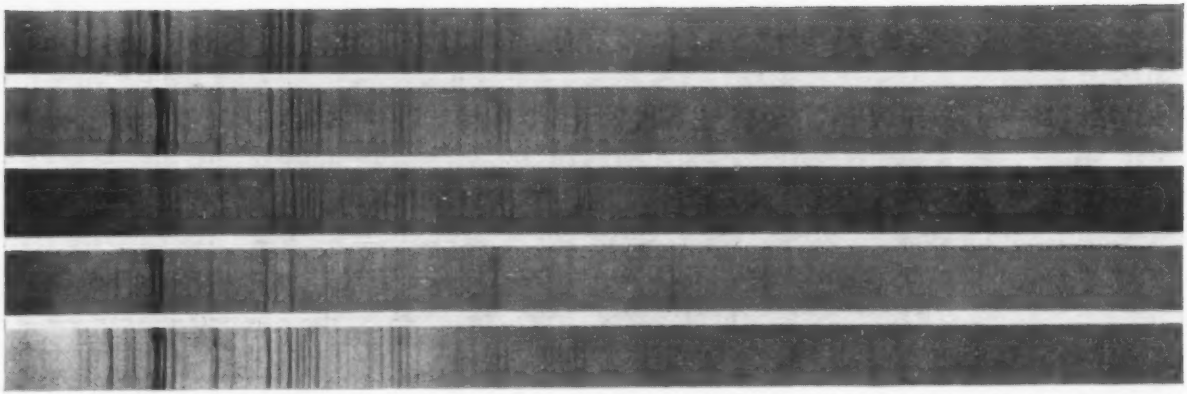

FIG. 4. X-ray powder photographs of phosphors with apatite-type crystal structure. (*a*) $3Cd_3(PO_4)_2CdCl_2$ Mn activated; (*b*) $3Ca_3(PO_4)_2CaF_2$ + 3% Sb; (*c*) $3Ca_3(PO_4)_2CaF_2$ + 3% Sb + 2% Mn; (*d*) $3Ca_3(PO_4)_2CaCl_2$ + 3% Sb + 2% Mn; (*e*) Calcium hydroxy (oxy) phosphate + Cu.

It cannot be said that any of the explanations offered are satisfactory and, in the present state of our knowledge, it would seem more fruitful to essay a "mechanism" in terms of the usual energy level diagram of the lattice assuming, for example, that the movement of electrons from the manganese ground level to the filled band is forbidden except as a two step process via the antimony ground level. It is true, of course, that excitation by cathode rays does not require the presence of the primary activator. It is probable that in this case direct excitation of the manganese atom is taking place. Simple energy considerations show that the manganese ground state is intermediate between that of the antimony level and the conduction band. In this connection, it is an interesting and significant fact that manganese alone rarely, if ever, produces photoluminescence in alkaline earth compounds, but appears to require the presence of a primary

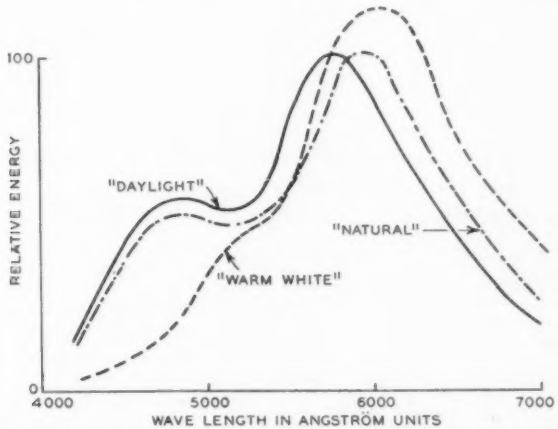

FIG. 5. Spectral energy curves of "Daylight," "Natural," and "Warm White" halophosphates.

activator. It is also significant that the photoluminescence of the primary activator is always of shorter wavelength than that of the secondary activator.

Excitation and spectral emission characteristics.—So far the only source of exciting energy which has been considered is short-wave ultraviolet of about 2537 Å. There is also appreciable excitation of the antimony activated materials in the low current density, low pressure discharge in pure neon by the neon resonance lines at 736 and 740 Å. Under long-wave ultraviolet, such as 3650 Å, most of the phosphors discussed emit a weak yellow or orange luminescence, if manganese is present, which tends to become somewhat stronger after repeated heating of the phosphor. This fluorescence differs from that excited by short-wave ultraviolet in that it is independent of the presence of a primary activator. High energy x-rays cause appreciable excitation of the phosphors, the luminescent color being similar to that given by 2537 Å ultraviolet. Cathode ray excitation of 6000 volts corresponds more to that of 3650 Å ultraviolet in that the

luminescence appears to be mainly associated with the manganese atoms rather than with the primary activator.

Fig. 5 shows the distribution of energy throughout the spectrum for three of the halophosphates used in British fluorescent lamps. The characteristic blue band associated with the antimony activator is, clearly, never com-

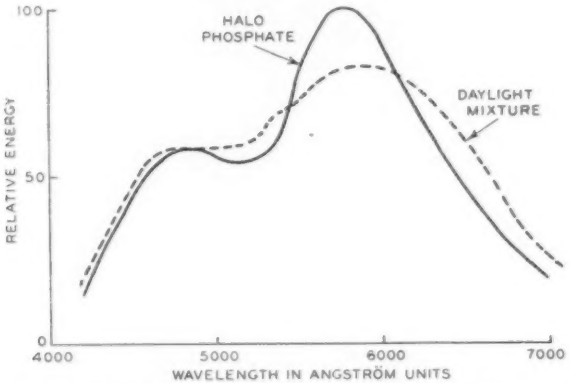

FIG. 6. Spectral energy curves of halophosphate and mixed powder "Daylight" phosphors.

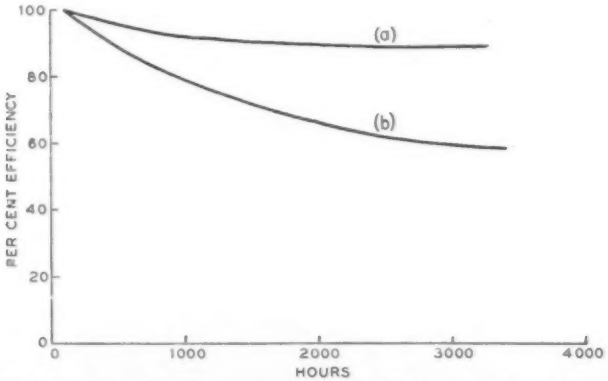

FIG. 7. Comparison of performance of 80 watt. 5ft lamps coated with: (*a*) "Daylight" halophosphate; (*b*) "Daylight" mixed powder.

pletely suppressed by the manganese and is visible even in the curve for the "Warm White" phosphor. The marked peak in the emission in the region 5800–6100 Å is a characteristic of most of the white halophosphates so far studied. Compared with white mixtures using zinc beryllium silicate phosphors, the emission in the red at 6500 Å and above is somewhat depressed, as shown in Fig. 6 which compares the spectral emission of halophosphates and mixed powder whites of "Daylight" color.

Performance.—Halophosphates, which are now well established in England, use relatively inexpensive chemicals and can, therefore, be produced at appreciably lower cost than zinc beryllium silicate and magnesium tungstate. The manufacturing convenience of having only one phosphor,

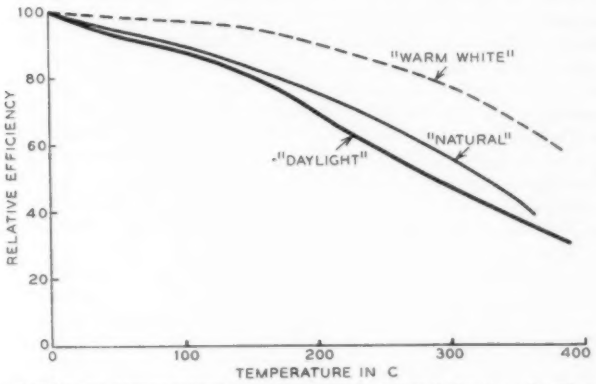

FIG. 8. Efficiency-temperature relationship for "Daylight," and "Warm White" halophosphates.

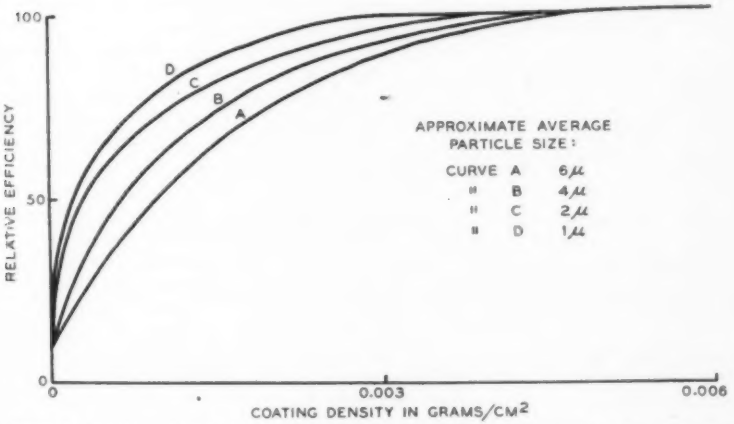

FIG. 9. Relationship between lamp efficiency and coating weight for halophosphates of different average particle size.

instead of the usual blended mixture, in the coating suspension is considerable, and the luminous performance, and particularly the lumen maintenance, of the halophosphates is excellent. Under conditions of low electrical loading, the efficiency and lumen maintenance of halophosphates and mixtures of zinc beryllium silicate and magnesium tungstate of corresponding color appear to be substantially the same for lamps processed

under similar conditions. As shown in Fig. 7, greatly improved luminous performance is obtained with halophosphates in 80 watt 5 ft lamps, which is the main British rating, where the current density in the lamp is about double that of the 40 watt 4 ft lamp. All the lamps, from which the data in Fig. 7 were obtained, were coated with normal commercial phosphors and were processed under closely similar conditions.

Percentage fall in light output has been deliberately stressed in these curves rather than absolute values of efficiency, since the latter is so much a function of the method of processing, the precise spectral distributions of the phosphors, and various other factors. As a matter of interest, however, the average value of the intial (100 hour) efficiency of these experimental lamps was approximately 50 lumens per watt for both phosphors.

Another characteristic of halophosphates, which is of particular importance in connection with their use in lamps of high electrical loading, is their good performance at the high bulb temperature attained by these lamps which may reach 80 C in enclosed fittings. The curves in Fig. 8 show the brightness-temperature relationship for "Daylight," "Warm White," and "Natural" color halophosphates. It is interesting to note that the "Warm White" phosphor, which has the highest manganese content, is the most temperature stable. Even in the worst case, the fall in brightness is at 100 C only about 10 per cent below that at 20 C.

As with other phosphors, particle size of halophosphates is an important characteristic in relation to performance in fluorescent lamps. The particle size depends, among other things, on the starting materials and the method of manufacture; the objective is always to make the powder as fine as practicable. Any desired particle size can, of course, be obtained by milling, and a certain amount of milling is always necessary to break up agglomerates and to incorporate the powder in the nitrocellulose binder. Milling cannot be carried beyond a certain point, however, without serious loss in efficiency, and the particle size must be kept as low as possible by taking steps during manufacture. Fig. 9 shows the relationship between lamp efficiency and coating weight for halophosphates of different average particle size. Particle sizes were derived from specific surface measurements and are, therefore, the average diameter of a spherical particle as derived from such measurement. It will be seen that the maximum efficiency can be achieved with phosphors of different particle sizes but that, as might be expected, the coarser the powder the greater the coating weight required.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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STREAMING POTENTIAL MEASUREMENTS WITH PHOSPHORS[1]

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ABSTRACT

Streaming potentials of phosphor surfaces and of pyrex glass surfaces have been determined with the aid of non-polarizable electrodes under conditions which promote varying degrees of adhesion of phosphor to glass. The materials and reagents were commercial products employed in the manufacture of television screens. Zeta potentials of the solid surfaces were calculated from the streaming potential data.

INTRODUCTION

The coating of glass with phosphor to produce fluorescent surfaces on cathode-ray tubes requires a medium which will promote adhesion of phosphor to glass. It is a common practice in the manufacture of television screens to use a mixture of potassium silicate and sodium sulfate as the adhesive (10, 11). While this mixture gives satisfactory results, either component alone is relatively ineffective. Indeed, tests in our laboratory with dilute potassium silicate solutions have revealed that in the absence of an addition agent such as sodium sulfate, the phosphor is strongly repelled by the glass (4).

The following describes the study made to clarify the mechanism of the action of the sodium sulfate in the system. The role of surface potential in this mechanism was investigated by conducting streaming potential measurements on pyrex glass and on a phosphor in the presence of (*a*) potassium silicate, (*b*) sodium sulfate, and (*c*) mixtures of these two substances.

EXPERIMENTAL METHODS AND MATERIALS

Apparatus.—A modification of the apparatus described by Briggs (1) for measuring the streaming potentials of packed cellulose diaphragms was employed (Fig. 1). In the present work, perforated platinum discs confining the materials under investigation were used only to make conductance measurements. For potential measurements it was found that the utilization of calomel electrodes connected to the system by potassium chloride-agar salt bridges served for greater accuracy and convenience in measuring. Platinum electrodes, because of their tendency to polarize, have not been applied very successfully to the measurement of streaming potentials. Briggs and others were forced to use an electrometer or other delicate measuring device in attempts to overcome this difficulty. Reyerson, Kolthoff, and Coad (9) reported satisfactory potential measurements with platinum electrodes using a potentiometer and sensitive galvanom-

[1] Manuscript received March 4, 1949. This paper prepared for delivery before the Philadelphia Meeting, May 4 to 7, 1949.

eter. It was found by us and also by Rabinov and Heymann (8) that even the use of a vacuum-tube voltmeter does not eliminate polarization difficulties. Reversible electrodes had been employed by Freundlich (2) and, more recently, by Jones and Wood (6) for measurements on capillary tubes. Briggs had found these inapplicable to diaphragm measurements because of the longer electrical path and high resistance involved. In the present work, it has been found possible to employ calomel electrodes with a potentiometer and galvanometer for measurements in which the specific conductivity of the solution was 0.0012 ohm^{-1}-cm^{-1} or greater. With more dilute solutions, the high resistance required the use of a high impedance measuring device. A vacuum-tube pH meter[2] having an emf scale was found to be suitable. In these cases, the higher streaming

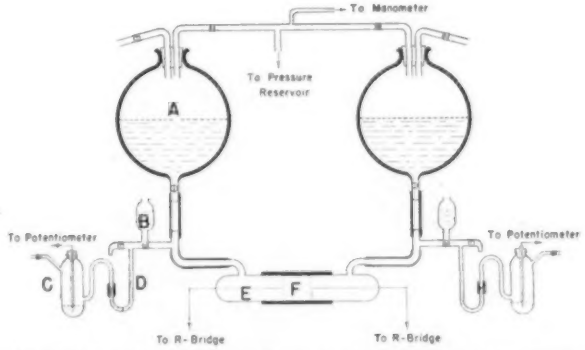

FIG. 1. Streaming potential apparatus. A—solution reservoir; B—reservoir for 1.0*N* KCl; C—1.0*N* calomel electrode; D—1.0*N* KCl—agar salt bridge; E—housing for platinum electrode; F—diaphragm material.

potentials obtained with the more dilute solutions compensated for the decreased precision of the measuring instrument.

The electrical circuiting was insulated to prevent stray currents. Where necessary, surfaces were coated with paraffin. Mercury-well contacts were substituted for switches. The calomel electrodes were enclosed within the pressure system. The pressure upon them set up an equal and opposite back-pressure which equalized the pressure across the agar bridges. Care was taken to have all air displaced from the calomel cells when filling. An arrangement was made for replacing the solution in the side-arm with 1.0*N* KCl when not in use in order to preserve the salt bridge concentration.

Diaphragm.—Various conventional methods were employed in an effort to confine the phosphor powder without leakage at the pressure gradients involved. None of the attempts met with success until a section of rubber tubing was employed as the cell compartment (Fig. 2). Each of the perforated platinum electrodes comprising the ends of the cell was covered

[2] Leeds & Northrup #7661.

with a sheet of filter paper[3] sandwiched between loosely meshed cotton gauze, which acted as a reinforcement. The rubber tubing which served as the cell compartment had the same diameter as the platinum discs and electrode housings. A tight fit that prevented leakage was obtained by using filter paper-gauze sandwiches large enough to overlap the electrode housings. The seals were made secure with a band of wire. To introduce

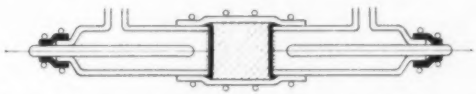

FIG. 2. Detail of diaphragm assembly. Small circles are cross-sections of wire reenforcement bands. Broken lines at ends of diaphragm represent perforated platinum electrodes, covered with filter paper and gauze.

the phosphor, the cell was clamped in a vertical position with the lower electrode in place. It was filled, while under suction to remove excess

[3] It is of interest to inquire into the effect of filter paper on the measurements. The filter paper and powder may be regarded as two streaming potential cells in series. The streaming potential of each will depend both on the zeta potential and on the pressure difference across it. The hydrostatic pressure drop across each portion will be proportional to its resistance to flow. Hence, if the flow resistance of the filter paper is a small proportion of the total flow resistance, its streaming potential will be a small fraction of the total. The electrokinetic equation

$$H = \frac{\zeta P \epsilon}{4\pi\eta K_s}$$

may be expressed as $H = \frac{k\zeta P}{K_s}$ where k combines all quantities which may be held constant at constant temperature.

If the flow resistance of the filter paper does not exceed 1 per cent of the total then

$$\frac{H_{\text{powder (p.)}}}{H_{\text{filter paper (f.)}}} \geqq \frac{100.\,\zeta_p K_{sf}}{1.\,\zeta_f K_{sp}}$$

For most solutions used in this study the ratio, K_{sf}/K_{sp}, had a value of unity. Measurements by Mr. S. W. Van Voorhis in our laboratory show that ζ for filter paper varies between -7 and -12 mv under the experimental conditions involved. The zeta potentials of the phosphor ranged between -11 and -53 mv. The largest error would be involved when the differences are greatest and may be approximated as follows:

Without filter paper, $H = k' \cdot 100(-53) = -5300k'$ (here k' allows P to be expressed as 100).

With filter paper, $H' = k' \cdot 99(-53) + k' \cdot 1(-7) = -5254k'$.

$$\text{Relative error} = \frac{-5300 - (-5254)}{-5300} = 0.87\%.$$

At lower values of ζ_p, this error approaches 0.5 per cent to 0.1 per cent.

With a pyrex wool diaphragm, which is extremely porous, the filter paper would form a high per cent of the total flow resistance and would introduce appreciable errors. Fortunately, the perforated platinum discs alone were capable of confining the glass wool, and no filter paper was used.

liquid, to a depth of about 1.5 cm by pouring in a slurry of the powder in 0.01*N* KCl. The second electrode with its filter paper-gauze covering in place was pressed into the rubber tubing against the powder and wired. Having the filter paper dry during this operation increased its strength and guarded against tears. The cell was made more rigid by wrapping it with friction tape enclosing glass rods.

Measurements.—The apparatus was tested by investigating the effect of pressure on the potential developed. The results (Fig. 3) agree with theory in that the ratio of streaming potential to pressure difference for a given cell is a constant. The measurements were made with the phosphor powder and 0.001*N* KCl at pressures between 10 cm and 40 cm of Hg. The values are corrected for zero pressure potential.

All results reported below were made at a hydrostatic pressure difference of 40 cm of Hg. This was a compromise between the pressure limitations

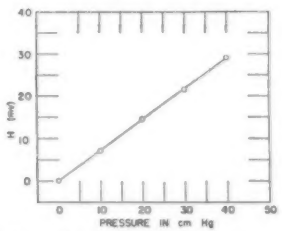

FIG. 3. Relationship of streaming potential to pressure difference for a phosphor diaphragm with 0.001*N* KCl.

TABLE I. *Effect of KCl concentration on zeta potential of phosphor*

Conc KCl	ζ (mv)
0.0001*N*	−11
0.001*N*	−12
0.01*N*	−12

of the apparatus and the desire for as high a pressure difference as possible in order to minimize the experimental error. Potential measurements were taken in each case with no flow in order to obtain a zero pressure correction value. This was of the order of one to two millivolts. The cell constant for pyrex wool diaphragms was obtained using 0.01*N* KCl since with this concentration of electrolyte surface conductance becomes negligible.[4] With phosphor diaphragms, solutions having a specific conductivity of 0.01 ohm^{-1}-cm^{-1} or greater were required for cell constant determinations. The streaming potential with 0.01*N* KCl served as the reference value for the other data. Evidence indicating that KCl has

[4] Although many investigators use 0.1*N* KCl to measure the cell constant, a much more dilute solution may suffice in many instances. Jones and Wood (6) found that the surface conduction in vitreous silica capillaries was negligible with solutions as dilute as 0.0001*N*. In the investigation covered in this paper, it was found that the cell constant for pyrex wool diaphragms was constant at least down to a dilution of 0.01*N* KCl.

very little effect on this system is seen in the relationship of zeta potential of phosphor to KCl concentration (Table I).

In making calculations, the Helmholtz-Briggs equation (1) was transformed to the following for convenience:

$$\zeta = 8.48 \times 10^6 \cdot \frac{Hk\eta}{Rx \cdot \epsilon \cdot P}$$

where ζ = zeta potential in millivolts.
H = streaming potential in millivolts.
k = cell constant in cm^{-1}.
η = viscosity in centipoises.
Rx = resistance across diaphragm in ohms.
ϵ = dielectric constant of H_2O (specific inductive capacity).
P = hydrostatic pressure difference in cm Hg.

Temperature varied during this investigation between 21 C and 31 C, and its effect upon viscosity, dielectric constant, and specific conductivity was considered when substituting the appropriate value in the equation. For the relationship of dielectric constant to temperature, the empirical equation of Linton and Maass (7) was used.

$$\epsilon = 79.2\,[1 - 4.28 \times 10^{-3}(t - 25) + 2.12 \times 10^{-5}(t - 25)^2 - 4.1 \times 10^{-7}(t - 25)^3]$$

where t = temperature in degrees centigrade.

According to preliminary measurements of the effect of potassium silicate on viscosity at the concentrations used, the values for these solutions vary only negligibly from pure water. The specific viscosity of the most concentrated silicate solution used, 0.62 per cent K_2O: 1.56 per cent SiO_2 was found to be 1.01 ± .01.[5] Accordingly, the values substituted were those for pure water.

Materials.—Phosphor powder:—R.C.A. #33-2-8 (P4) phosphor, a zinc sulfide-zinc silicate composition.

Pyrex Glass:—Pyrex Wool made by Owens-Corning Fiberglas Corporation.

Potassium Silicate:—Kasil No. 1, manufactured by the Philadelphia Quartz Company (Analysis: 7.8% K_2O, 19.5% SiO_2; molecular ratio, K_2O:3.92SiO_2). A stock solution of the silicate was prepared fresh daily by diluting 80 ml of the commercial sample to one liter with distilled water.

Sodium Sulfate:—Analytical Reagent Grade, Mallinckrodt Chemical Works.

EXPERIMENTAL RESULTS

The method was found to be rapid, easy to execute, and reproducible, the standard deviation of the zeta potential being ±1 to ±2 millivolts for several runs on any single diaphragm. The standard deviation of the zeta potential as obtained on different diaphragms of the same material was ±2 to ±3 millivolts depending on the absolute value of the zeta potential. Results obtained independently by Mr. S. W. Van Voorhis using this method agree closely with those of the investigators.

The data is presented graphically in the accompanying figures. Each

[5] Courtesy of the Philadelphia Quartz Company.

point represents an average of at least four runs and more often of six or eight. Zeta potentials for both glass and the phosphor were found to be negative in all cases, but are plotted in opposite directions from a zero ordinate in order to show the relative repulsion under varying conditions.

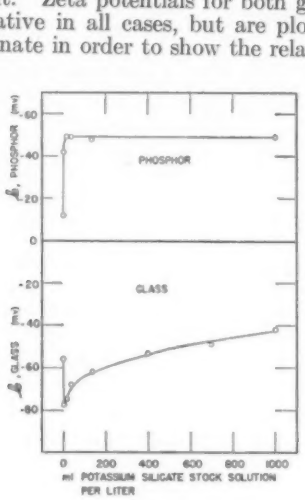

FIG. 4

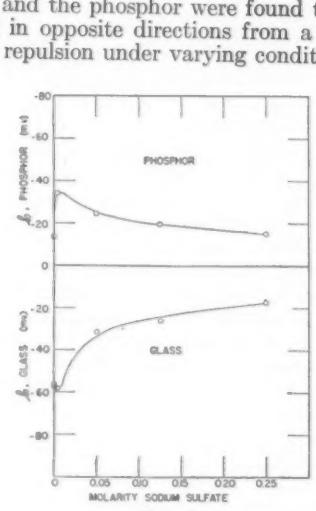

FIG. 5

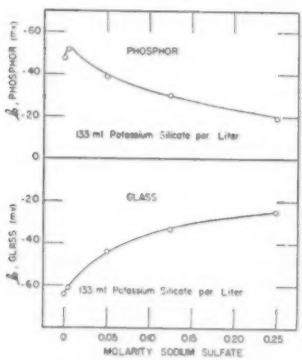

FIG. 6

Fig. 4 shows the effect of concentration of potassium silicate upon the two surfaces. It is seen that even a small amount of potassium silicate increases the zeta potential of the phosphor, and that even at the highest concentrations, electrical repulsion should be strong. The falling off of the potential on glass with higher concentrations possibly is due to a crowding in of the diffuse layer by potassium ions which become more abundant and exert a so-called screening effect. This effect is absent in the case of the phosphor.

The effect of sodium sulfate concentration in the absence of potassium silicate is shown in Fig. 5. It is obvious that at higher concentrations both surface potentials are diminished to a level at which interaction may be facilitated. However, there is poor adhesion of the phosphor to the glass in the presence of sodium sulfate alone.

The effect of the mixture of potassium silicate and sodium sulfate upon the surface potentials is shown in Fig. 6. In this case, the Kasil concentration was maintained at a constant value (133 ml of stock solution per liter) and the concentration of sodium sulfate varied. The potentials decreased to a level allowing chemical interaction but not quite to the extent which they did in the absence of Kasil. With the mixture, however, good adhesion occurs.

DISCUSSION

The information obtainable from these measurements, both regarding zeta potential and adsorption, are compatible with the following mechanism for the adhesion process. It is seen that sodium sulfate lowers the surface potentials sufficiently to enable the glass and phosphor particles to come into close proximity. Nevertheless, adherence is extremely weak for this case, the conclusion being that direct glass to phosphor bonding forces are insufficient to affect the union. This points to the function of potassium silicate as a bonding agent. In the presence of Kasil and in the absence of sodium sulfate, the mutual repulsion, manifested visibly, prevents the particles from getting close enough to interact. That silicate must be adsorbed on both surfaces is evidenced by the rise in potential with low concentrations of Kasil. In the case of the phosphor, the adsorption was found strong enough to resist long washing with distilled water, and with 0.01*N* KCl, the potential remaining higher than −40 mv.

When sodium sulfate is added to the system, it accelerates the adhesion in two ways.

1. It lowers the zeta potential of both the glass-silicate surface and the phosphor-silicate surface so that the particles may approach each other closely enough to allow bond formation. This effect is not specific for Na_2SO_4, but is due to high electrolyte concentration affecting a compression of the boundary layer.

2. The sodium sulfate promotes bonding of the surfaces, presumably by formation of oxygen bridges between the silicate adsorbed on the surfaces (4).

$$\equiv Si{-}OH + HO{-}Si\equiv \xrightarrow{Na_2SO_4} \equiv Si{-}O{-}Si\equiv + H_2O$$

The same type of polymerization occurs in silica gel formation (5). Experiments in our laboratory on the effect of ions of the lyotropic series on silicates (3) have shown that sodium sulfate is capable of causing alkali silicates to gel.

SUMMARY

1. It was found that potassium silicate increased the zeta potential of phosphor and of glass surfaces.

2. Sodium sulfate alone, and when mixed with potassium silicate, lowered the zeta potential of these solid surfaces.

3. The role of sodium sulfate in promoting the adhesion of phosphor to glass is discussed.

4. An improved method for measuring streaming potentials of powders is described.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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THE RATE OF SOLUTION OF HIGH PURITY ALUMINUM IN VARIOUS BASES[1]

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ABSTRACT

A series of dissolution experiments of high purity aluminum (99.998%) in KOH, $Ba(OH)_2$, $Sr(OH)_2$, $Ca(OH)_2$, $Mg(OH)_2$, and NH_4OH solutions of different concentrations was carried out. The reproducibility of the experiments was nearly the same as in the case of NaOH reported in a previous paper (1). For low concentrations, the rate of dissolution in monovalent bases increases with the cube root of the concentration, while in divalent bases, the rate increases as the square root of the concentration. At higher concentrations, the rate of reaction is directly proportional to the concentration. The solution rate-concentration curve for NH_4OH solutions does not follow either of these relationships. The dissolution in NH_4OH, $Mg(OH)_2$, $Ca(OH)_2$, and $Sr(OH)_2$ is hampered by the formation of insoluble reaction products. In very dilute solutions all the strong bases act similarly, while at concentrations higher than 1*N* the rate of attack decreases in the following order: NaOH, KOH, and NH_4OH.

INTRODUCTION

Many investigations have been described in the literature concerning the rate of dissolution of aluminum in various bases. However, all these investigations were made with aluminum of lower purity than is now available. As in the case of NaOH (1), many contradictions exist between the results of the various investigators. Maass and Wiederholt (2) found that the rate of solution of aluminum in $Ca(OH)_2$ is higher than in NaOH or even in $Ba(OH)_2$, a result that was partly confirmed by Bohner (3). Centnerszwer and Wittandt (4) came to contrary conclusions.

There have been many attempts to investigate the dissolution of aluminum of lower purity in $Ca(OH)_2$ solutions. The papers of Allen and Rogers (5), Heyn and Bauer (6), Goldberg (7), Siebers (8), Maass and Wiederholt (2), Buschlinger (9), Mertens (10), Centnerszwer and Wittandt (4), and Bohner (3), may be mentioned here. Only some of them, (2), (3), and (4), may be regarded as quantitative.

The first dissolution experiments of aluminum in NH_3 solutions were made by Wöhler (13). Then followed Dagger (14), Göttig (15), Smith (16), Hale and Forster (17), Bailey (18), Calvet (19), Jefries (20), Davies (21), Matignon and Calvet (22), Centnerszwer (23), Bohner (3), Centnerszwer and Wittandt (4), and others. Further work was done with 99.95

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per cent aluminum by Röhrig and Roch (24) and qualitative experiments with 99.998 per cent aluminum by Kühnrich (25).

EXPERIMENTAL PROCEDURE

Aluminum (R. Gadeau) (1*a*) and reagents of the highest purity were used for these experiments. Preparation of the samples and the apparatus used for the measurement of the dissolution rate were the same as previously described (1). The volumes of evolved hydrogen were corrected to 0 C, 760 mm Hg, and dryness; the rates of dissolution were measured by these volumes and expressed in $mm^3/min\ cm^2$ of dissolving aluminum surface $\left(V = \frac{\Delta v}{\Delta t F}\right)$. It could be proved that the hydrog enevolution measurements were accurate indications of the solution rate. The loss of hydrogen due to diffusion through the rubber tubing connections was insignificant and did not affect the results. The rates for the first five-hour periods excluding the irregular starting period, usually the first 30 to 60 minutes, were chosen for comparison. The stirring speed was about 120 ± 5 revolutions per minute.

EXPERIMENTAL RESULTS AND DISCUSSION

The rate of dissolution in KOH.—No references could be found in the literature concerning the dissolution of high purity (99.998%) aluminum in KOH ("Kahlbaum" *pro anal.*) nor are there exhaustive experiments on record in the case of lower purity aluminum.

Sixteen tests were made, some of them lasting over a period of 28 to 30 hours. The final results are summarized in Fig. I. It follows from the data that the rate of solution in KOH is proportional to the cube root of the concentration up to 2*N* KOH:

$$V = 18.9 \sqrt[3]{N} \qquad \text{(I)}$$

At higher concentrations the curve follows a straight line:

$$V = 12.5 + 7.5N \qquad \text{(II)}$$

The agreement of the experimental results with these equations is shown in Fig. 1. The surface of the corroded plate was very similar to that obtained after dissolution in NaOH. It was glossy and the crystallites could be clearly distinguished by their borders and their metallic lustre. The rate of dissolution in KOH at the beginning of the reaction was practically identical with the rate in NaOH (1), 18.9 and 18.85 $mm^3/min\ cm^2$ of hydrogen, respectively. At higher concentrations, aluminum reacts with NaOH 11, and KOH 7.5. This higher reactivity with NaOH could be proven by putting a plate from a run in 5*N* KOH in an apparatus with 5*N* NaOH. In the course of 3 hours the rate of solution approximately doubled and was still increasing.

The rate of dissolution in $Ba(OH)_2$.—Maass and Wiederholt (2) made some runs using aluminum of lower purity. They found that $Ba(OH)_2$ solutions acted more slowly than solutions of NaOH or KOH. As our observations showed opposite results and the deviations from the average in parallel runs reached 20 per cent, 22 dissolution experiments were performed with two kinds of $Ba(OH)_2$, "$Ba(OH)_2 \cdot 8H_2O$ Merck *puriss.*" and

"$Ba(OH)_2 \cdot 8H_2O$ Merck *pro anal.*" Two curves could be drawn through all experimental points as shown in Fig. 2 (broken lines). Because of the limited solubility of $Ba(OH)_2$ in water the highest possible concentration of the base was $0.5N$. The dissolution reaction begins with a higher aver-

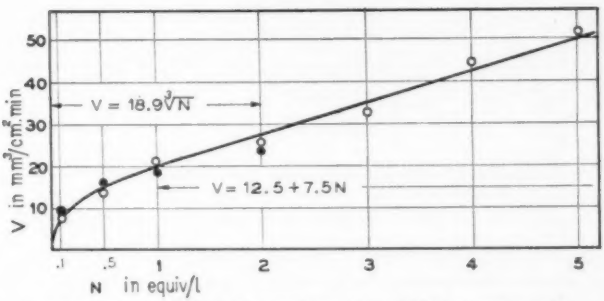

FIG. 1. The rate of solution of high purity Al *vs.* KOH concentration. ●—Calculated points, ○—Observed values.

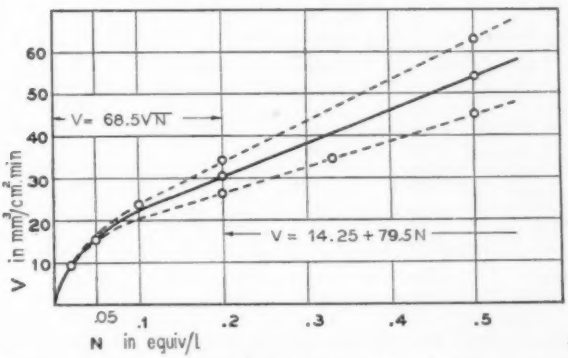

FIG. 2. The rate of solution of high purity Al *vs.* $Ba(OH)_2$ concentration. The experimental points obtained lie on the broken lines. The solid line represents the average values.

age rate than either NaOH or KOH. The rate is proportional to the square root of the concentration up to $0.2N$:

$$V = 68.5\sqrt{N} \qquad \text{(III)}$$

The rate is linear between $0.2N$ and $0.5N$:

$$V = 14.25 + 79.5N \qquad \text{(IV)}$$

The rate was considerably higher than in the previous two cases; compare the slope constants of the straight line. The agreement between experimental data and the equations (III) and (IV) is shown in Fig. 2.

The surfaces of the plates after $Ba(OH)_2$ tests were as shiny as if they had been polished. The borders of the grains could scarcely be distinguished. In some cases, the surfaces were partly covered with a very thin gray layer which could be easily removed with wet filter paper. Usually this layer caused a lower rate of solution.

The rate of dissolution in $Sr(OH)_2$.—The $Sr(OH)_2$ solutions were prepared from a pure reagent (Merck). The normality of the concentrated solution was $0.17N$. The reaction rate in dilute $Sr(OH)_2$ was slightly higher than in $Ba(OH)_2$, *i.e.* up to $0.05N$:

$$V = 78\sqrt{N} \qquad \text{(V)}$$

At higher concentration the reaction rate is indicated by:

$$V = 14.4 + 41.7N \qquad \text{(VI)}$$

The average experimental and calculated results are listed in Table I.

The affected surfaces were fairly bright, but not as bright as after dissolution in $Ba(OH)_2$. Contrary to previous results, the rate of dissolution

TABLE I. *Dissolution rate of 99.998% aluminum in various bases of 25 C—average values*

Base	Concentration (Normal)	Rate observed	Rate calculated	Δ	Equation
$Sr(OH)_2$	0.02	11.9	11.0	+0.9	V
"	0.05	16.4	17.4	−0.8	"
"	0.05	16.4	16.5	−0.1	VI
"	0.1	18.4	18.6	−0.2	"
"	0.165	21.4	21.3	+0.1	"
$Ca(OH)_2$	0.021	3.0	2.9	+0.1	
"	0.044	3.9	4.1	−0.2	
$Mg(OH)_2$	$\sim 10^{-4}$	0.5–0.6			

of aluminum in $Sr(OH)_2$ showed a slight tendency to decrease during the separate tests. This may have resulted from the formation of insoluble surface layers indicated by dull appearance of the plates after exposure.

The rate of dissolution in $Ca(OH)_2$ and $Mg(OH)_2$.—In $Ca(OH)_2$ solutions, the rate of dissolution of aluminum falls rapidly during the first 30 minutes of reaction and then it diminishes steadily, being nearly constant only during the 60–360 minute period of reaction. After 1500 minutes the rate is only half as great as during this steady period. After the tests, the surface of the plates were covered with a white, tenaceous porous layer under which the bright aluminum was visible. The layer was insoluble in acetic acid and probably consisted of a mixture of calcium aluminate and aluminum hydroxide. The rate of solution in $Ca(OH)_2$ was approximately proportional to the square root of concentration:

$$V = 19.5\sqrt{N} \qquad \text{(VII)}$$

The average results are listed in Table I. They show that the dissolution

of aluminum in $Ca(OH)_2$ solutions was slower than in other strong bases. This is in accordance with the findings of Centnerszwer and Wittandt (4). No doubt the reason may be explained in terms of the formation of insoluble surface layers on the aluminum during the reaction.

The solubility of $Mg(OH)_2$ in water is low, and the solutions contained about 0.8×10^{-4} to 2×10^{-4} gram equivalents per liter (11) (12). The initial reaction rate is low and slowly decreases with time and remains approximately constant during the period of the 60–360 minute reaction period. The average rate was approximately 0.55 $mm^3/min\ cm^2$ (Table I). After 50 hours, the rate of reaction approached zero. The reaction surface was covered with a white layer which was soluble in hydrochloric acid, but not in acetic acid.

The rate of dissolution in NH_3 solutions.—The tests in NH_3 solutions were carried out in a similar manner as in the previous experiments, except that the hydrogen was collected in the gas burets over NH_3 solutions

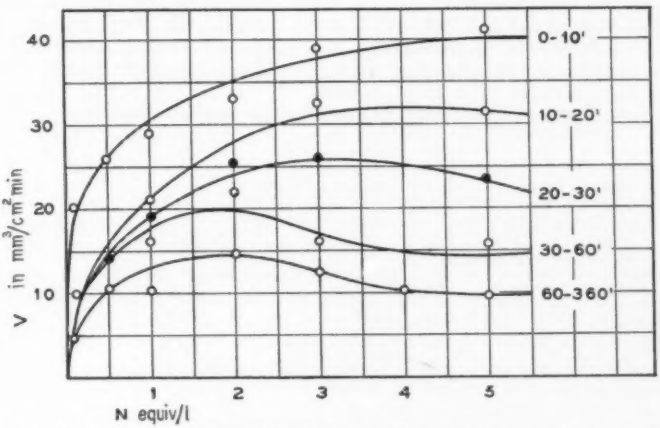

FIG. 3. The rate of solution of high purity Al *vs.* NH_3 concentration. 0–10′—average rate during the first 10 min; 10–20′—average rate during the second 10 min, etc.

of the same concentrations as were being used for the respective experiments.

For every test the reaction rate gradually decreases with time as shown in Fig. 3. The rate of dissolution decreases faster in more concentrated solutions than in dilute solutions. The maximum rate of solution after one hour exposure was observed in the approximately $2N$ ammonium hydroxide solutions. This is in accordance with the observations of others working with aluminum of lower purity, although maxima at various concentrations were found by Göttig at $5.6N$, Bailey at $0.5N$, Davies at $1.2N$, Calvet-NH_3 at medium concentrations, and Röhrig at $2.9N$.

The formation of a maximum may be explained as follows: During the reaction aluminum hydroxide is formed which partially sticks to the surface of the plates, retarding the rate of solution. Presumably a denser surface layer is produced in ammonium hydroxide solutions of higher concentra-

tion so that the activity of the solvent is hampered. The surface layers are not as easily seen as in the cases of $Ca(OH)_2$ or $Mg(OH)_2$.

CONCLUSIONS

The present experimental data lead to the following statements concerning the reactivity of bases with 99.998 per cent aluminum:

If the formulas for the rate of reaction (I), (III), (V), and (VII) and for NaOH (1) are valid in the region of very low concentrations of the bases, then their reactivities decrease in the following order:

KOH, NaOH, $Sr(OH)_2$, $Ba(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, and NH_4OH

In very dilute solutions the calculated rates for the five first bases (0.92, 0.87, 0.78, 0.69, 0.60 $mm^3/min\ cm^2$) do not differ appreciably; it may be said that these bases will react equally.

For 0.05*N* solutions the bases in order of decreasing activity are: $Sr(OH)_2$, $Ba(OH)_2$, KOH, NaOH, and NH_4OH. The differences in the reactivities of $Sr(OH)_2$ and $Ba(OH)_2$ are not large, and they may exchange places. This is also true for KOH and NaOH. During the first minutes of reaction, NH_4OH acts more rapidly than either KOH or NaOH.

For solutions stronger than 1*N* the order is: NaOH, KOH, NH_4OH.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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CHEMICAL PROPERTIES OF THE INTERMETALLIC COMPOUNDS Mg_2Sn AND Mg_2Pb[1, 2]

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ABSTRACT

The intermetallic compounds Mg_2Sn and Mg_2Pb constitute two members of an analogous series of four stoichiometric compounds that magnesium forms with elements of the fourth group of the periodic table. The study of the physical and chemical properties of these compounds was undertaken to provide data concerning the constitution of such compounds, and also to provide a more complete understanding of corrosion mechanisms in alloys.

The electrical properties have been reported elsewhere. Certain chemical properties are reported herewith. They include oxidation rates at high and low temperatures, galvanic potentials, rates of reaction in inorganic electrolytes, and a previously unreported form of crystallographic disintegration, occurring in distilled water and having a possible relation to stress corrosion cracking.

INTRODUCTION

No systematic or quantitative measurements of the oxidation rate of Mg_2Sn or Mg_2Pb have been reported in the literature. Qualitative observations on alloys containing high concentrations of the compounds were recorded by those studying the equilibrium diagrams.

Most recently, Hume-Rothery (1) reported that Mg_2Sn is oxidized in air (of unknown humidity) to stannous and magnesium oxides, both components being oxidized where, separately, neither is extensively attacked. Tammann and Ruhenbeck (2) and Grube (3) observed alloys containing Mg_2Sn and Mg_2Pb; they report that the alloys are stable in a desiccator containing phosphorous pentoxide for periods exceeding one year. Both compounds, however, are said to disintegrate to a black powder in "normal atmospheric air," Mg_2Sn forming a mixture of MgO and SnO, and Mg_2Pb breaking down more rapidly to form hydrated oxides of magnesium and lead corresponding to the formula $(PbO \cdot 2MgO) \cdot 3H_2O$. Grube (4) observed that the spontaneous oxidation of Mg_2Pb in air is accompanied by a sensible evolution of heat, a fact which we confirm. The compound Mg_2Sn is less reactive in this respect.

Thus, the literature reveals little beyond the fact that both compounds are comparatively unstable in air containing water vapor. The mech-

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[2] This investigation constitutes part of a thesis submitted by W. D. Robertson to the Department of Metallurgy, Massachusetts Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science.

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anism of corrosion is ascribed to the fact that the protective film normally covering magnesium is destroyed by the addition of tin or lead, but no other chemical or electrochemical mechanism is postulated.

Galvanic potentials of magnesium-tin and magnesium-lead alloys were measured by Kremann and his co-workers (5) (6). The electrolyte was magnesium sulfate and the standard of reference was tin or lead. Few experimental details were given, but they found a difference of potential between magnesium-rich alloys and tin- or lead-rich alloys of about 120 millivolts. The change in potential is assumed to take place at the composition corresponding to the compound but, in reality, there was a gap of ten atomic per cent in this region not represented by the alloys investigated although, on the excess tin and lead side, the compound was approached within about two per cent. Another investigation by Jenge (7), on the magnesium-lead system, confirms the above work and indicates a difference of 100 millivolts between the excess magnesium and excess lead alloys.

No data exist on reaction rates of the compounds in inorganic electrolytes and, hence, there is no reported discussion of the reaction mechanism.

The electrical properties of the compounds, which have a bearing on the chemical and electrochemical properties, were recently investigated (8). Briefly, it was found that Mg_2Sn, even though composed of two metals, does not behave as a metal. It is an electronic semi-conductor with an electrical resistivity of 42,000 microhm-cm at 20 C compared to 11.5 microhm-cm for tin and 4.46 microhm-cm for magnesium. The corresponding lead compound, Mg_2Pb, is a normal metal with respect to electrical conduction, but it has a comparatively high resistivity of 220 microhm-cm at 20 C.

One of the objectives of this research was to supply information on the mechanism of corrosion in alloys as affected by the type of metallic bonding. The Mg_2Sn and Mg_2Pb intermetallic compounds are salt-like, brittle, and hard, with relatively high heat of formation. The heat of formation of Mg_2Sn is 17,300 calories per mole (9) and for Mg_2Pb 12,600 calories per mole (10). They represent, therefore, an extreme type of chemical bonding in metal systems, the effect of which on chemical reactivity can be estimated from the data presented below.

EXPERIMENTAL PROCEDURE

The materials and methods employed to produce the alloys and compounds have been reported elsewhere in detail (8). Redistilled magnesium and electrolytically purified tin and lead were used. The component metals were melted in graphite and cast under argon into a chilled graphite mold. Chemical analyses for both components and for silicon, carbon, and nitrogen indicated that the principal impurities were silicon, which varied from 0.01 to 0.002 per cent, and nitrogen, which ranged from 0.003 to 0.005 per cent. The attainment of the stoichiometric proportions corresponding to Mg_2Sn and Mg_2Pb was verified by metallographic examination which, in view of the almost complete absence of solid solubility, was a more sensitive test for the homogeneous single phase compounds than the reported chemical analyses.

Oxidation measurements were conducted on weighed quantities of screened powder, produced by crushing the brittle compound in a mortar until the resulting powder passed through 28 mesh screen and was retained on 100 mesh. This procedure provided adequate surface area and clean cleavage faces, and it was experimentally determined that duplicate powder samples showed the same weight gain within one per cent. Thus, all experimental oxidation curves are directly comparable since the same weight of powder was used. A conservative calculation of the area indicated 80 cm^2 per gram of powder and a comparison of the rate of hydrogen evolution in sodium chloride with a solid specimen of known apparent area indicated 60 cm^2 per gram. Therefore, the surface area of 2 gram powder samples employed in oxidation tests was approximately 140 cm^2. However, because the estimate of area is only approximate, the results are not reported in terms of unit area.

For the measurement of oxidation as a function of humidity and time, the powder was weighed in dry Petri dishes to ± 0.0001 gram and placed in desiccator containers in which a known, constant humidity was maintained by means of saturated aqueous solutions of calcium chloride, sodium acid sulfate, zinc sulfate, and water over which the humidity is respectively 32, 52, 90, and 100 per cent at 20 C. The specimens were weighed periodically until the weight-increment-time curves were well established.

High-temperature oxidation rates were determined by measuring the volume of gas absorbed at constant temperature and pressure with a calibrated gas burette and mercury leveling bulb. The powder sample was contained in a glass tube which was evacuated and immersed in a salt bath previously heated to the temperature at which the experiment was to be conducted. When the sample reached the desired temperature, indicated by a thermocouple in contact with the sample, the gas previously passed over ascarite and calcium chloride was admitted and absorption measured as a function of time. A sketch of the apparatus is given in Fig. 1.

Galvanic potentials were measured with reference to the silver-silver chloride electrode, the mercury-mercuric oxide electrode, and the normal calomel electrode, the latter protected by an intermediate agar salt bridge.

Instantaneous potentials were measured by bringing the capillary tip of a glass tube containing NaCl and the Ag-AgCl electrode into contact with approximately one square millimeter of freshly cleaved alloy surface. Potentials were averaged over several such areas on a single surface.

Potentials were also determined for the alloys totally immersed in air-saturated electrolytes. Surface preparation of the alloy included final abrasion with No. 0 emery paper. For measurements in NaOH solution, brief immersion in nitric acid was followed by neutralization in NaOH, allowing magnesium hydroxide to come in contact with the alloy surface. Values of potential were recorded after reaching a steady state, usually some hours after immersion. A vacuum tube galvanometer was used to avoid polarization.

Reaction rates in aqueous electrolytes were determined by measuring the volume of hydrogen evolved as a function of time. This criterion of reaction was adopted after demonstration that hydrogen was the sole gaseous reaction product. The salt solution was prepared and placed in reservoir A (Fig. 2), which was then evacuated with a water aspirator to

a pressure of about five millimeters, thereby removing most of the dissolved air. At the same time, the gas burette, B, was evacuated with the specimens in place. The burette stopcock, 1, and the reservoir stopcock, 3, were closed and tank hydrogen admitted through the fritted glass dispersion disc immersed in the salt solution. The hydrogen was passed through the solution until the manometer pressure was several centimeters above atmospheric pressure when the relief cock, 4, was opened and the passage of hydrogen continued to sweep out remaining traces of air and insure saturation. The relief stopcock was closed and the hydrogen-saturated solution admitted to the burette and the specimen through cock 6 which was then left open.

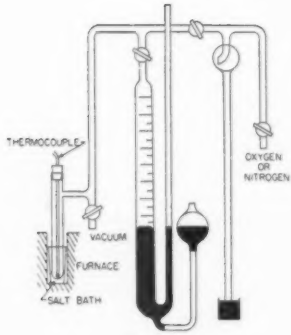

FIG. 1

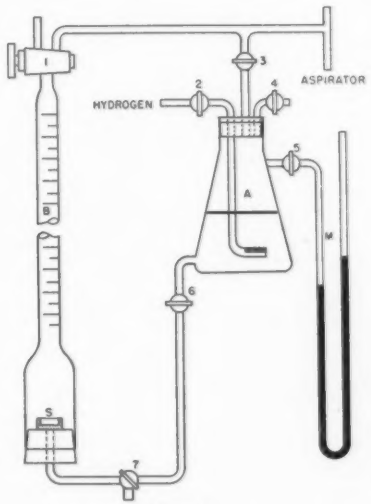

FIG. 2

FIG. 1. High-temperature oxygen and nitrogen absorption apparatus
FIG. 2. Hydrogen evolution apparatus for determining corrosion rates

The specimens, S, were cut from the alloy rods in the form of round discs. The sides and bottom were coated with hot sealing wax, leaving the top surface exposed to the solution. This surface was ground flat on a fine carburundum wheel immediately before starting the test. The initial area was obtained from the diameter of the rod and was about 0.8 cm^2.

EXPERIMENTAL RESULTS AND DISCUSSION

Low temperature oxidation.—Fig. 3 and 4 show the cumulative weight gain of Mg_2Sn and Mg_2Pb powders exposed to oxidation in atmospheres containing varying amounts of water vapor.

With respect to Mg_2Sn, it is apparent that humidity does affect the initial rate $\left(\frac{dw}{dt}\right)$. However, the subsequent rate decreases practically to

zero in a period of 36 hours and, below at least 90 per cent relative humidity, is independent of the humidity. Contrary to statements in the literature, this apparent stability of pure Mg_2Sn is fully confirmed by additional qualitative observations which indicate that the powdered compound retains its bright bluish appearance after months of exposure to the prevailing laboratory atmosphere in which the humidity varies over a wide range.

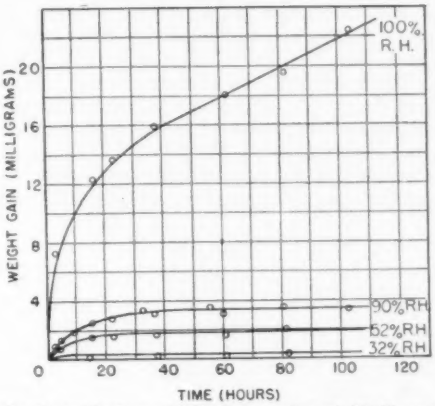

FIG. 3. Atmospheric oxidation of Mg_2Sn powder at 20 C as a function of time and humidity.

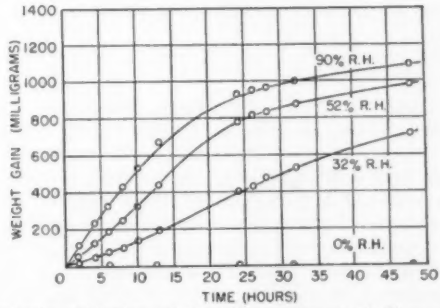

FIG. 4. Atmospheric oxidation of Mg_2Pb powder at 20 C as a function of time and humidity.

At 100 per cent relative humidity, however, the rate of oxidation is of a higher order; the initial rate is greater and, instead of decreasing rapidly to zero, the rate remains finite and constant. The change in oxidation rate at 100 per cent relative humidity is associated apparently with the fact that condensed water is present on the specimen and vessel walls whereas, at lower humidity, the dew-point is not reached within the range of small temperature fluctuations to which the sample is subject. *Water*, distinct from *water vapor*, causes a crystallographic breakdown of the compound

along octahedral cleavage planes, by a mechanism that will be described in detail later. As a result, new, unoxidized planes are continuously produced, the exposed area of compound continuously increases, and the oxidation continues with time.

The corresponding curves for Mg_2Pb likewise show the effect of humidity on the initial rate. But, unlike Mg_2Sn, the rate does not go rapidly to zero but remains finite and essentially independent of humidity.

There is an obvious difference in magnitude between the oxidation-time curves of the two compounds, indicated by their weight gain ratio for equivalent area and time (Table I). The apparent difference arises from the fact that the tin compound, in the absence of condensed water, evidently forms a protective film which limits further reaction, whereas, the lead compound reacts to completion, forming hydrated oxides of lead and magnesium. If the formula $(PbO \cdot 2MgO)\ 3H_2O$ is assumed for the final reaction product as indicated by Grube (3), the calculated maximum increase in weight of the sample originally weighing 2.96 grams is 1180 milli-

TABLE I

Relative humidity per cent	Weight gain ratio $\frac{Mg_2Pb}{Mg_2Sn}$ per unit area in 48 hr
32	2400
52	505
90	300

grams; the data at 90 per cent relative humidity show a gain of 1080 milligrams in 48 hours with a slowly continuing reaction, not inconsistent with this end product.

High temperature oxidation

Oxygen absorption (N. T. P.) by Mg_2Sn powder as a function of time and temperature is shown in Fig. 5, together with pure magnesium for comparison. Two grams of $-28/+100$ mesh powder of Mg_2Sn were used in each run and 0.975 grams of magnesium powder, approximately equivalent in area to the Mg_2Sn powder. For Mg_2Pb, the data are given in Fig. 6. The sample of equivalent area in this case weighed 2.96 grams.

Evidently, two distinct processes are involved: (*a*) a comparatively slow constant rate of absorption, and (*b*) a discontinuous change to a high rate which decreases in time. The latter process apparently corresponds to the burning of magnesium and, in accord with this, a white powder is produced.

Of more interest is the constant rate observed before burning sets in. The logarithm of this rate constant is a linear function of the reciprocal absolute temperature (Fig. 7), and it is possible, therefore, to express the rate by an Arrhenius equation of the form:

$$k = A\, e^{-\frac{E}{RT}}$$

where E is the apparent energy of activation, equal to 22,100 cal per mole for Mg_2Sn, and A is a constant equal to 2.1 cm^3 per hour.

While it is evident that some regular mechanism is involved, expressible in familiar terms by the Arrhenius equation, it is more difficult to specify the particular process, or processes, to which the activation energy applies.

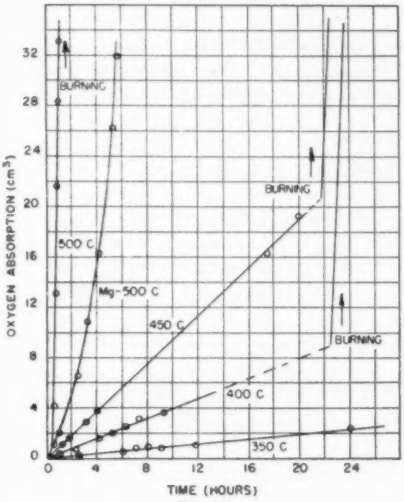

FIG. 5

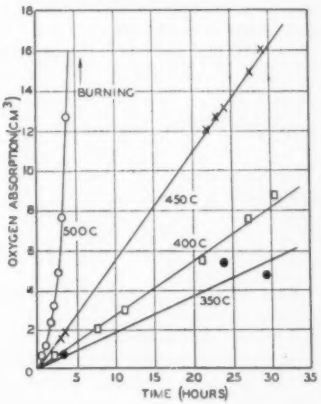

FIG. 6

FIG. 5. High-temperature oxidation of Mg_2Sn powder as a function of time and temperature.

FIG. 6. High-temperature oxidation of Mg_2Pb powder as a function of time and temperature.

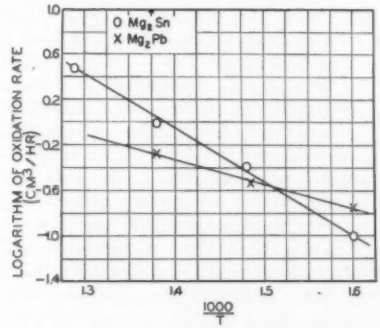

FIG. 7. Temperature dependence of reaction rates for Mg_2Sn and Mg_2Pb in oxygen.

The absorption reaction is heterogeneous, involving solid and gaseous reactants, and the above apparent activation energy is a function of the specific surface as well as the reacting substances.

It should, however, be noted that the same relationship was observed by Leontis and Rhines (11) for magnesium at comparable temperatures, except that the activation energy was 50,500 calories per mole instead of 22,100 calories per mole. Therefore, on the basis of experimental activation energies alone, it appears that less energy is required to initiate oxidation of Mg_2Sn than magnesium.

The same linear oxidation rate is characteristic of Mg_2Pb but the magnitude is generally lower. Thus, for comparison, the volume of oxygen absorbed in ten hours at 350 C to 450 C, and in one hour at 500 C by equivalent areas is as follows:

Compound	Volume of oxygen absorbed (cm^3)			
	10 hours			1 hour 500 C
	350 C	400 C	450 C	
Mg_2Sn	1	4	9.6	29.0
Mg_2Pb	1.8	2.7	5.4	1.1
Mg				2.0

The oxidation rates have only limited quantitative significance, yet it is clear, except at 350 C, that the rate for Mg_2Pb is generally lower. Furthermore, ignition does not occur below 500 C after more than twice the time interval required for Mg_2Sn.

The effect of temperature on the apparent reaction rate constants of Mg_2Pb is expressible in terms of the preceding exponential function (Fig. 7) where E is 10,350 calories per mole. At present, there is no complete explanation for the low activation energy. One factor which has not been considered is the fact that Mg_2Sn cleaves along the octahedral planes while the Mg_2Pb specimens employed had no pronounced cleavage plane and, consequently, initial oxidation of the former may take place on a definite crystallographic plane which will influence the rate. Another factor, because of the presence of lead or tin, is change in nature of the protective oxide film first formed on oxidation (11).

With respect to nitrogen, the comparative positions of magnesium and the compounds are reversed. Both Mg_2Sn and Mg_2Pb absorb negligible quantities of nitrogen below 600 C, whereas, an equivalent area of magnesium absorbed 60 cm^3 per hour at 550 C. Similarly, Mg_2Pb did not absorb measurable quantities of nitrogen up to 500 C, even in the presence of water vapor which has been shown to break down the compound.

Summarizing, it appears that at elevated temperatures Mg_2Sn oxidizes more rapidly than either Mg_2Pb or pure magnesium. In nitrogen, on the other hand, magnesium reacts more rapidly than either of the two compounds. At low temperatures, and in the presence of water vapor, Mg_2Pb oxidizes more readily than either Mg_2Sn or magnesium.

Galvanic potentials.—The steady-state and initial potentials of the magnesium-tin series of alloys in different electrolytes are shown in Fig. 8.

First, considering only the single phase electrodes, magnesium, Mg_2Sn, and tin, in the steady state, it is evident that in sodium chloride the compound is cathodic (noble) with respect to pure magnesium and anodic

(active) with respect to tin. In sodium fluoride, magnesium assumes the same potential as the compound, presumably that associated with the film of magnesium fluoride which is precipitated in contact with the surface. The action of sodium hydroxide, on the other hand, is to reverse the relationship so that magnesium is cathodic to the compound and the latter is equal in potential to pure tin.

Responsibility for shift of steady-state potential with environment seems to rest more with the behavior of pure magnesium or tin than with the compound. The potential of Mg_2Sn, within about 0.1 volt, is the same whether in NaCl, NaF, or NaOH.

The potentials of alloys intermediate in composition between the components and the compound are compromise galvanic potentials determined

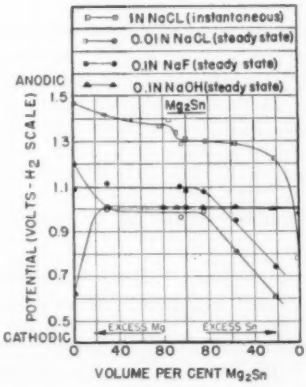

FIG. 8

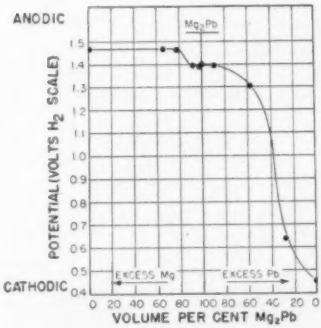

FIG. 9

FIG. 8. Galvanic potential of magnesium-tin alloys in sodium chloride, sodium fluoride, and sodium hydroxide as a function of alloy composition.

FIG. 9. Instantaneous galvanic potentials of magnesium-lead alloys in 1*N* NaCl as a function of alloy composition.

by the polarizing properties of the two phases in a given electrolyte. The two-phase alloys constitute a short circuited cell composed of the anodic component metal or compound (depending on the electrolyte) and the cathodic phase. The polarizing current reduces the anodic potential and increases the cathodic potential, usually one more than the other, until, in the steady state, they become equal in the absence of resistance, and the two-phase alloy surface assumes a single potential or so-called corrosion potential with reference to an external standard. When polarization is largely at the anode, the corrosion potential is that of the cathode and vice versa.

The potentials of the two-phase alloys in Fig. 8 are the corrosion potentials, and it is evident that the shape of the curve connecting the three single phase values will depend on the character of the polarizing function and the area of each phase because, as tin is added to magnesium, the relative area of the two phases changes in accordance with the phase diagram.

In the steady state, the relationships are such that there is no sharp discontinuity at the composition corresponding to the compound. For the instantaneous curve only, there is a difference of the order of 75 millivolts which is similar to that found by Kremann (5) (6). Apparently, the effect of the magnesium-rich phase becomes negligible when the volume fraction in excess of the compound decreases to less than ten per cent.

The instantaneous potentials of the magnesium-lead system (Fig. 9) are similar to magnesium-tin, except that pure magnesium and Mg_2Pb have more nearly the same potential in sodium chloride. Again, the change in potential, 75 millivolts, takes place on the magnesium side of the compound in a composition range not covered by previous workers who extrapolated values for higher concentrations of magnesium to the compound composition.

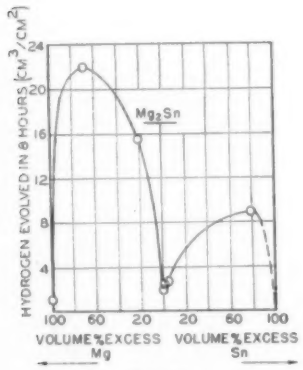

FIG. 10

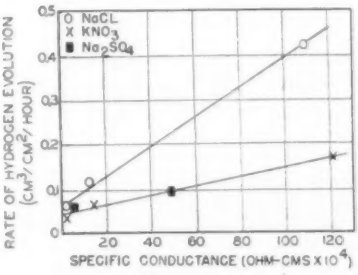

FIG. 11

FIG. 10. Corrosion rates of magnesium-tin alloys in 1*N* NaCl as a function of magnesium and tin in excess of Mg_2Sn.

FIG. 11. Rate of corrosion of Mg_2Sn at room temperature in NaCl, Na_2SO_4, and KNO_3 solutions as a function of specific conductance of the electrolyte.

Reaction rates in sodium chloride

The volume of hydrogen liberated by the reaction of magnesium-tin alloys in 1*N* sodium chloride is not a simple function of composition. For the purpose of comparing the different alloys and components, comprising single and polyphase structures, the volume of hydrogen liberated in eight hours per unit apparent area is shown in Fig. 10.

It is evident that the corrosion rate of the three single-phase specimens, magnesium, Mg_2Sn, and tin, is lower than that of the two-phase alloys on either side of the compound; the rate for Mg_2Sn is higher than magnesium, though not greatly so. Evidently, also, the presence of excess magnesium has more effect on the rate than excess tin. The results are in accord with the galvanic mechanism of the corrosion of two-phase alloys in which the two phases have different potentials and the alloy is the metallic conductor in a short-circuited galvanic cell.

These results provide some measure of the rate of reaction in sodium

chloride, but do not indicate the mechanism by which the compound liberates hydrogen or the nature of the final products. For this purpose, 0.1 gram of Mg_2Sn powder (−28 +100 mesh) was placed in the hydrogen evolution apparatus (Fig. 2) with deaerated- and hydrogen-saturated 1*N* sodium chloride. The powder was allowed to react to completion, shown by the cessation of hydrogen evolution (3 days), and the volume of hydrogen collected was observed for comparison with the amount calculated on the assumption that only the magnesium was involved.

The following results were obtained:

Calculated volume of H_2 corresponding to magnesium in 0.1 gram of Mg_2Sn	= 25.0 ml
Measured volume of hydrogen	= 24.9 ml
Deviation	= 0.1 ml

Additional data were obtained by allowing another weighed specimen of powder to react completely in sodium chloride and in the absence of air. After the hydrogen evolution had ceased, the reaction products were washed free of sodium chloride with distilled water and, finally, with 25 ml of acetone, and then dried in a desiccator containing anhydrous calcium chloride. The dry products were weighed with the following results:

Weight of Mg_2Sn powder	0.1654 g
Weight of corrosion products	0.2347 g
Weight gain	0.0693 g

Assuming that the products of reaction are magnesium hydroxide and metallic tin, the calculated weight gain is 0.068 gram, which deviates from the experimental value by 1.8 per cent where, for comparison, the assumption of magnesium hydroxide and stannous oxide results in a calculated gain of 0.0833 gram, a deviation of 17 per cent from the experimental value. Because no other combination of products is in such close agreement with experiment, it is our conclusion that the reaction is of the following form:

$$Mg_2Sn + 4H_2O \rightarrow 2Mg(OH)_2 + Sn + 2H_2$$

A similar experiment conducted in the presence of air, in an open beaker filled with 1*N* sodium chloride, produced different results. Thus,

Weight of Mg_2Sn powder	0.3019 g
Weight of corrosion products	0.4453 g
Weight gain	0.1440 g

This increase in weight cannot be reconciled with the preceding hypothesis, but corresponds closely to the weight gain calculated on the assumption of magnesium hydroxide and stannous oxide as reaction products, namely, 0.150 gram.

Therefore, the equation for the reaction in the presence of oxygen is:

$$Mg_2Sn + 4H_2O + \tfrac{1}{2}O_2 = 2Mg(OH)_2 + SnO + 2H_2$$

It is probable that the initial reaction is identical to that which takes place in the absence of air, but the liberated finely divided tin is subsequently oxidized by the dissolved oxygen.

The reaction of Mg_2Pb with aqueous sodium chloride yielded somewhat less than an equivalent quantity of hydrogen. In two experiments, the volume of hydrogen evolved from a known weight of Mg_2Pb in sodium chloride was less than the calculated amount by 10 and 20 per cent, respectively. The reaction time was seven days and, during the last day, there was no measurable evolution of hydrogen. The change in weight of the products with respect to the initial weight of compound was intermediate between that calculated for magnesium hydroxide and lead, and magnesium hydroxide and PbO; the former assumption was 11 per cent lower, and the latter 11 per cent higher than the experimental weight gain.

It appears plausible that these results are explained by premature oxidation of the specimen of compound in humid air of the laboratory before insertion into the hydrogen evolution chamber. Such oxidation is difficult to avoid because of the extreme reactivity of Mg_2Pb.

The above experiments on Mg_2Sn show the reaction and the final products. However, sodium chloride does not appear in the equations and the rate of reaction with distilled water, while not zero, is relatively small and of the order of 1/20 that in 1*N* sodium chloride. The role of sodium chloride, therefore, remains to be demonstrated.

If the mechanism of the reaction is electrochemical, as it seems to be, the rate should be proportional to the resistance of the electrical path. A given potential difference will determine the flow of current and the transport of matter. The electrolyte forms part of the electrical path, and, in general, has higher electrical resistivity than the compound (approximately 13 ohm-cm for 1*N* NaCl *vs.* .04 ohm-cm for Mg_2Sn). Other factors being constant, the corrosion rate in terms of the volume of hydrogen evolved per unit area should then be proportional to the conductivity of the electrolyte. Furthermore, if the rate is a function of resistance only, other electrolytes having the same specific conductivity should produce the same rate.

To test this hypothesis, the initial rate, in terms of the volume of hydrogen per unit area per hour, was measured in varying concentrations of sodium chloride, potassium nitrate, and sodium sulfate. It should be emphasized that these rates were obtained in the presence of air and are not, therefore, directly comparable with the preceding values. They are, however, comparable with each other since they were all obtained under identical conditions.

The rate, as a function of specific conductance, is shown in Fig. 11, and it is apparent that there is a direct relationship between conductivity and rate. It is also apparent that there is a specific ion effect because two straight lines are obtained, one for sodium chloride and one for potassium nitrate and sodium sulfate.

It appears, therefore, that the function of the electrolyte is that of a conducting path for the transference of ions, the rate of which depends on the current and, consequently, the conductance. The mechanism accounting for the specific effect of chloride ions is not certain, except for the recognized fact that chlorides constitute one of the most active corrosive agents.

Although magnesium in the Mg_2Sn lattice is presumably positively charged and tin negatively charged, it is difficult to see how the rate of electrochemical action involving anodes and cathodes of so small dimensions is dependent on solute ions in the bulk of electrolyte. It seems more

likely that blocks of surface atoms differing slightly in composition or structure act as anodes and cathodes, these areas possibly shifting from place to place as surface conditions change.

This view receives support from studies of reaction rates of liquid amalgams. Wagner and Traud (12) showed that the potential of a zinc amalgam in hydrochloric acid is approximately the potential of mercury polarized cathodically by a current equivalent to the reaction rate of the amalgam. This proved that the overvoltage of hydrogen on mercury controls the corrosion rate of the amalgam, and that the reaction is electrochemical. It appears plausible at first glance to assume anodes and cathodes distributed at random on any liquid-metal surface, yet the electrochemical action in this instance also occurs, apparently, over blocks of atoms rather than individual atoms. Observations of Brönsted and Kane (13), for example, indicated that sodium amalgam reacts evolving hydrogen largely at the middle portion of a stagnant amalgam surface, rather than uniformly over all the surface.

It should also be noted in Fig. 11 that both lines extrapolate to a limiting value of approximately 0.05 $cm^3/cm^2/hr$, representing the corrosion rate in pure water. Direct measurements of this rate failed, owing to physical breakdown of the compound to progressively smaller geometrical fragments with a resulting large increase in area, a problem discussed in detail below. In salt solutions, the more rapid surface reaction took place without observable crystallographic breakdown.

Corrosion cracking of Mg_2Sn and relation to stress corrosion cracking.—The continuous subdivision, into smaller fragments, of polycrystalline specimens used in the attempted corrosion-rate measurements in distilled water, suggested similar tests using single crystals of Mg_2Sn. The single crystals behaved in like manner and disclosed a phenomenon that does not appear to have been reported previously. The fragments of single crystals were geometric forms: three-sided pyramids and rhombohedra derivable from the octahedral crystal structure of Mg_2Sn. A photograph of these fragments has been published elsewhere (14).

Large crystals of the compound were produced by remelting the polycrystalline substance in argon and cooling at a rate of 20 C per minute through the melting point. The resulting cast rods, $\frac{3}{8}$ inch by 4 inches (.95 by 10.2 cm) long, could be easily fractured (cleaved) to produce a bright, plane cleavage face across the entire cross section and at some angle to the axis of the rod. Subsequent experiments were conducted with sections cleaved from these large crystals.

In distilled water, 35 per cent hydrogen peroxide, sodium hydroxide and ammonium hydroxide, the crystals of Mg_2Sn disintegrate to geometrical fragments which continue to subdivide in time, but the geometrical form is always preserved. It is probable that other reagents also produce cracking, but of the reagents tried, only those listed above were found to have this property.

Qualitative observation of the disintegration rate in sodium hydroxide indicated that it is a function of the hydroxyl ion concentration. In 5, 1.0, and 0.1 per cent sodium hydroxide, the first appearance of cracking occurred in 2, 5, and 10 hours, respectively. Cracking in distilled water took place in 18 to 24 hours, whereas in ammonium hydroxide about 48 hours were required, possibly because the alkalinity of NH_4OH is less than

that of saturated $Mg(OH)_2$, the latter forming when the compound corrodes in water. The presence of liquid water, distinct from water vapor, appears to be necessary because there was no evidence of cracking when crystals were exposed to atmospheres containing water vapor up to 90 per cent relative humidity.

The presence of hydrogen as reaction product was not a necessary condition to cracking as was found by mounting a specimen as cathode in .02*N* NaOH and comparing it with a similar specimen mounted as anode in the same electrolyte. At the applied current density of .05 amp/cm^2, the cathode fractured much less rapidly than the anode. The difference in fracturing rate may be caused by differences in local concentration of hydroxyl ion at anode and cathode in accord with observations in NaOH solutions mentioned above. Further experiments are planned bearing on this observation.

The slow cooling of the crystals precluded large residual stress and, in any case, the initial and continuing fracturing would tend to relieve whatever stress was present. Therefore, the fracturing appears to be an extreme case of trans-crystalline corrosion cracking in the absence of appreciable applied or residual stress.

FIG. 12. Unit cell of Mg_2Sn or Mg_2Pb

Owing to the geometric character of the resulting fragments, the mechanism is obviously related to the crystal structure of the compound. The structure of Mg_2Sn is that of CaF_2 with the magnesium ions occupying the fluorine positions and the tin ions the positions of the calcium ions. Thus, the lattice is face-centered cubic with respect to tin (Fig. 12). The magnesium ions are situated at the centers of the eight cubes into which the unit cell may be subdivided. The (111) planes are the cleavage planes across which the cohesion is least and constitute one of the planes of centers for tin ions, the centers of the magnesium ions being slightly elevated above the tin ion plane. Since all the geometric forms into which the crystal disintegrates are derivable from the octahedron bounded by (111) planes, it appears that the action of water in splitting the crystal is one of hydration of the magnesium ions, thereby creating local lattice disturbances and attendant stresses that destroy the bond between the octahedral planes. Finite fragments are obtained, possibly owing to the fact that the crystal is not perfect and water is drawn in between certain preferred planes rather than into all planes equally. Allied with this mechanism, the formation of a corrosion product between cleavage planes may result in a pressure that mechanically splits the crystal.

One would expect Mg_2Pb to act similarly, but the reaction rate in water

was high, obscuring transgranular penetration if any occurred. Furthermore, single crystals were not obtained using the same procedure as for Mg_2Sn.

It is apparent that this phenomenon may be related to certain cases of so-called stress corrosion cracking in metals. There is increasing evidence that the "season cracking" of brass, for example, is associated, in part, with metallurgical factors inherent to the alloy itself instead of with impurities at the grain boundary. For example, single crystals of brass in ammonia also crack by stress corrosion, although grain boundaries are absent, and the critical applied stress necessary for cracking of a polycrystalline brass has been reduced to lower and lower limits (15).

The usual mechanism ascribes growth of stress-corrosion cracks to electrochemical action between material at the base acting as anode and the wall acting as cathode. In the spontaneous cracking of Mg_2Sn, such a mechanism may also apply, although the possibility of ion hydration mentioned before is also possible. The latter mechanism seems reasonable in view of the action in plastics of specific solvents which by their solvating effect on the component organic molecules cause similar stress cracking. The affinity of magnesium ions in Mg_2Sn for water is certainly pronounced enough to induce similar critical stresses in Mg_2Sn. There is possibility also, of course, that galvanic action between magnesium and tin ions of the Mg_2Sn lattice forms corrosion products that generate the necessary stress for failure along preferred planes. Should a crack of this kind initiate in a commercial alloy, whatever the details of mechanism, it is obvious that presence of applied or residual tensile stresses in the metal, although not necessary for the initiation of the crack, can account for subsequent propagation of the crack and failure of the alloy. In this sense, the above observations indicate that stress corrosion cracking of some metals may have its origin in compounds like Mg_2Sn that crack spontaneously when exposed to a simple corrosive environment like water.

CONCLUSIONS

1. Oxidation measurements at room temperature, as a function of time and humidity, show that the rate of oxidation of Mg_2Sn below 100 per cent relative humidity goes to zero after a small initial surface reaction. Under the same conditions, Mg_2Pb reacts to completion to form hydrated oxides of magnesium and lead.

2. High-temperature oxidation of both Mg_2Sn and Mg_2Pb, in the range 350 C to 550 C, is a linear function of time, and the reaction rates are an exponential function of the reciprocal absolute temperature; the activation energy for the oxidation of Mg_2Sn is 22,100 calories per mole and 10,350 calories per mole for Mg_2Pb.

3. Neither of the two compounds absorbs measurable quantities of nitrogen below 500 C where, for comparison, magnesium absorbs nitrogen readily.

4. Galvanic potential measurements as a function of time and alloy composition show that potential relations are dependent on the electrolyte; in chlorides, Mg_2Sn is less active than magnesium but more so than tin; in fluorides, magnesium and Mg_2Sn have the same potential; and in alkaline solutions, the compound and tin are equal.

5. The rate of reaction of Mg_2Sn in potassium nitrate and sodium sulfate

is seemingly dependent on the conductance of the electrolyte only; in chlorides, there is an additional specific ion effect. The reaction in the absence of air is:

$$Mg_2Sn + 4H_2O = 2Mg(OH)_2 + Sn + H_2$$

with tin in a finely divided state. In air (oxygen), the tin is further oxidized to stannous oxide.

6. In distilled water, sodium hydroxide, hydrogen peroxide, and ammonium hydroxide, single crystals of Mg_2Sn break down into geometric fragments—pyramids and rhombohedra—all of which are derivable from the octahedral cleavage planes of the intermetallic compound crystal system. It is possible than an analogous mechanism is operative in the corrosion cracking of certain alloys and that the cracking may *initiate*, therefore, independent of applied or residual stress.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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ATTEMPTS TO ELECTRODEPOSIT TANTALUM[1]

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ABSTRACT

The various methods for the electrodeposition of tantalum from aqueous and nonaqueous solutions which are recorded in the literature are reviewed and examined critically. The authors found that they were unable to electrodeposit tantalum from any of the baths described. Attempts to plate tantalum and tantalum alloys from numerous other aqueous and nonaqueous solutions were also unsuccessful. Electrodeposition from fused baths is not included in the review or experimental work.

INTRODUCTION

The successful electrodeposition of tantalum, particularly from an aqueous solution, would almost certainly be considered a major accomplishment and tantalum plating would probably rank with chromium plating in importance. The properties of tantalum, especially its resistance to most chemical reagents, make it an important and rather unique metal. Published information concerning the electrodeposition of tantalum is very meager and only a few articles on the subject are to be found in the literature. This paucity of information is understandable since it is quite probable that most, if not all, of the attempts to electrodeposit tantalum from aqueous solutions have met with failure and there is, of course, a natural reluctance to publish negative results.

The purpose of this work is to examine critically the claims for the electrodeposition of tantalum from aqueous and nonaqueous plating baths and to investigate as completely as possible other likely baths, except fused baths, for the plating of tantalum and its alloys. Even though the results obtained are negative, it seems desirable to report them in order that future investigators in this field may profit by the results.

PREVIOUS WORK

Perhaps the first claim for the electrodeposition of tantalum from a plating bath which was not a fused bath was made by Broughall (1), who in 1928 patented a liquid ammonia bath. In 1933, Grenagle (2) was granted a patent on a process for electroplating tantalum from a bath containing tantalum(V) chloride dissolved in acetonitrile. In a patent issued in 1934, Pokorny and Schneider (3) claimed that thin layers of tantalum, as well as molybdenum, tungsten, and vanadium, could be electrodeposited from strongly alkaline solutions. Isgarischew and Prede (4) attempted to plate tantalum from a number of different aqueous solutions. They claimed success with solutions prepared by extracting fusions of tantalum(V) oxide in potassium pyrosulfate with aqueous glucose, salicylic acid, or resorcinol. These claims were examined by Holt (5) who reported that the thin plates,

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which were obtained from baths of this type after a longer period of electrolysis, were cathode deposits of platinum which had entered the bath through corrosion of the platinum anodes. The patent of Armstrong and Menefee (6) claims the electrodeposition of alloys of tantalum with tungsten and nickel from aqueous plating baths which are essentially fluoride-tartrate solutions.

EXPERIMENTAL

The general plan followed in the experimental work was to check the most promising of the plating baths recorded in the literature by preparing and using them according to the directions given. Then, modifications in bath composition and electrolysis conditions were tried. Finally, numerous other possible plating solutions which suggested themselves were tried. The experimental work was logically divided into two parts, aqueous solutions and nonaqueous solutions.

Aqueous solutions

The Armstrong and Menefee patent (6).—One of the several tantalum alloy plating baths proposed in this patent contains 40 g/l of tungstic acid, 35 g/l of tantalum(V) oxide, 20 g/l of nickel chloride, 85 g/l of ammonium hydrogen fluoride, 60 g/l of tartaric acid and varying amounts of sodium hydroxide solution. Optimum conditions given are a bath temperature of 65 to 70 C, a pH of 1 to 8 or more, and a cathode current density(C.C.D.) of 0.6 to 55 amp/dm^2. An alloy electrodeposited from this bath was claimed to contain 25.8 per cent tantalum, 39.8 per cent tungsten, and 34.4 per cent nickel.

In our experimental work, baths of the type described above were prepared. It was found necessary to use unignited tantalum(V) oxide in order to obtain a clear bath solution. Varying amounts of sodium hydroxide solution were used to control bath pH. Electrolyses were carried out with platinum anodes, a copper cathode, a bath temperature of 70 C and a C.C.D. of 7.7 amp/dm^2. A large number of electrolysis runs were made at pH values ranging from about 2.5 to 6. Bright metallic cathode deposits were obtained from baths in the lower pH range, but no tantalum was detected in these plates, either by chemical or spectrographic means. The alloys were found to contain only nickel and tungsten. At a pH higher than 5, the tantalum in the bath started to precipitate as a hydrated oxide, and on electrolysis the amount of precipitate increased. When this partially precipitated bath was electrolyzed, the somewhat metallic deposit was impregnated with tantalum oxide. When boric acid was substituted for tartaric acid in preparing the bath, the tantalum(V) oxide was only slightly soluble.

Additional evidence about this type of bath was obtained by making an analysis of an alloy-plate sample given to this laboratory several years ago. This alloy plate was presumably produced according to the patent specifications and, according to the label, was a tantalum-tungsten-nickel alloy plated on brass. Since it was not possible to determine the weight of the alloy alone, an analysis of the plate and basis metal was made. A complete quantitative analysis showed the presence of tungsten, nickel, copper, zinc, and a trace of iron, the recovery being slightly more than the

weight of the sample taken. The tungsten (VI) oxide residues from the analysis were examined carefully for tantalum by the method of Schoeller (7). In no case was the presence of tantalum noted.

The patent also claims that, in the absence of nickel salts, this type of bath yields an alloy containing only tungsten and tantalum. To check this claim a bath of the following composition was prepared: Ta_2O_5, 20 g; H_2WO_4, 60 g; NH_4HF_2, 85 g; $H_2C_4H_4O_6$, 65 g; H_2O, 800 ml. When the bath was electrolyzed at the recommended C.C.D., 35 amp/dm^2, no metallic deposit was obtained. When 20 grams of $NiCl_2 \cdot 6H_2O$ were added to the bath, electrolysis gave the usual nickel-tungsten alloy deposit.

Citrate solutions.—The citrate solutions were somewhat similar to the citrate bath used for the electrodeposition of tungsten alloys (8). Potassium tantalate was prepared for this bath by fusing 2 grams of tantalum(V) oxide with 4 grams of potassium hydroxide. The melt was extracted with a solution containing 12.5 grams of ammonium citrate. About 0.5 grams of $NiSO_4 \cdot 6H_2O$ were added to the extract and the total volume made up to 100 ml with water. Electrolysis of this solution gave a cathode deposit of nickel, with no tantalum present. Various bath pH values were tried without success and it was observed that as the acidity was increased the tantalum in the bath precipitated as a hydrated oxide.

Oxalate solutions.—The complex compound of tantalum which forms in aqueous oxalate solutions appears to be fairly stable in slightly acid solutions. For the preparation of a possible plating bath, 1 gram of tantalum(V) oxide was fused with 7 grams of potassium pyrosulfate, and the cooled melt was extracted with 75 ml of hot saturated ammonium oxalate solution. About 0.5 gram of nickel sulfate was then added; the resulting solution had a pH of 2.5 at 70 C. On electrolysis a very thin scaly deposit, embedded with white oxide of tantalum, was obtained. Very little nickel was electrodeposited at this pH. When ammonium hydroxide was added to give a pH of 5, no change was noted in the thin cathode deposit obtained; also, at this pH, hydrated tantalum oxide started to precipitate from the bath during electrolysis.

Carbonate solutions.—A carbonate solution as a possible plating bath was prepared by fusing 1 gram of tantalum(V) oxide with 5 grams of potassium carbonate and extracting the melt with a solution containing 25 grams of potassium carbonate and 2 grams of potassium hydrogen carbonate. The undissolved Ta_2O_5 (about 0.4 g) was filtered off and the filtrate made up to 100 ml with water. Electrolysis of this solution gave no cathode deposit. After about 0.5 gram of nickel sulfate was added to the solution, electrolysis gave a thin deposit containing nickel but no tantalum. When iron(II) sulfate was substituted for the nickel salt, the bath on electrolysis gave a deposit of iron.

Hydrofluoric acid solution with a mercury cathode.—The final attempts to electrodeposit tantalum or its alloys from aqueous solutions were made using hydrofluoric acid solutions with a mercury cathode. The electrolyte was approximately 4*N* hydrofluoric acid saturated with potassium tantalum fluoride. Electrolysis was carried out in a polystyrene cell at a C.C.D. of about 18 amp/dm^2 and a temperature of about 90 C. After 2 hours of electrolysis, the mercury cathode was perfectly clean and was found to contain no tantalum.

The above described solutions include about all of the known compounds and complexes of tantalum which are soluble in aqueous solutions. The number is quite limited because of the great tendency of tantalum compounds to undergo hydrolysis, and the consequent instability of the solutions. To explore further the possible electrodeposition of tantalum the remaining tests were made with nonaqueous solvents. It should be mentioned that no attempt was made to check the liquid ammonia work of Broughall (1).

Nonaqueous solutions

Preparation of tantalum(V) chloride.—The tantalum compound used for this experimental work involving nonaqueous solutions was tantalum(V) chloride, $TaCl_5$. It was prepared by passing chlorine over either pure tantalum powder or a mixture of 2 parts of tantalum(V) oxide plus 1 part of sugar charcoal heated in a sillimanite tube in an electric furnace. Tantalum powder was most convenient for this preparation. Air in the tube and pyrex glass collecting bulbs was first removed by passing purified nitrogen through the system. When the temperature of the furnace reached about 400 C, the flow of dried chlorine was started. After the bulk of the tantalum chloride had distilled into the collecting tube, the temperature of the furnace was gradually raised until the reaction was complete. It was found that the yield of the chloride was higher when the flow of chlorine was fairly rapid at the start of the reaction and then somewhat slower after most of the product had distilled over. This technique seemed to prevent appreciable backward flow of the tantalum chloride into the combustion tube, which was considerable if the flow of chlorine was too slow. When the light yellow tantalum chloride had been distilled into the pyrex collecting bulb with the aid of a Bunsen burner, the bulb was sealed off to keep the chloride from contact with air and moisture.

Acetonitrile.—Attempts to repeat the work of Grenagle (2) using acetonitrile as a solvent for tantalum(V) chloride proved unsuccessful. The plating bath described in this patent is acetonitrile containing one per cent potassium hydrogen fluoride and ten per cent tantalum(V) chloride. Bath temperatures of 0 to 100 C and cathode current densities of 2 to 10 amp/dm^2 are suggested. The chloride dissolved readily in dried and redistilled acetonitrile, but it was not found possible to dissolve the amount of potassium hydrogen fluoride suggested. Electrolysis at room temperature and current densities ranging from 2 to 10 amp/dm^2 produced nothing but a white powdery compound which settled to the bottom of the cell. No metallic cathode plate was observed.

Glacial acetic acid.—Tantalum(V) chloride was found to dissolve readily in glacial acetic acid, but the solution was a very poor conductor. When nickel was introduced into the bath by using a nickel anode, the conductivity was only slightly improved and no cathode deposit was obtained.

Glycerol.—Tantalum(V) chloride was found to be somewhat soluble in glycerol and the solution had an appreciable conductivity at temperatures slightly above 100 C. Electrolysis using platinum anodes and a copper cathode gave no definite cathode deposit. On continued electrolysis, the cathode became covered with a crust of carbonaceous material due to decomposition of the bath.

Pyridine.—Tantalum(V) chloride was found to dissolve readily in dry redistilled pyridine. When electrolysis was carried out with graphite

anodes and a copper cathode, the conductivity of the bath was initially very good, but it soon dropped off to almost zero. The copper cathode was attacked by the solution and became coated with a brown, gum-like substance. When an iron cathode was used, there was no observable corrosion of the electrode, but the same gum-like film was formed. Anhydrous nickel chloride was soluble in the solution, but on electrolysis no cathode deposit was obtained.

Thionyl chloride.—Tantalum(V) chloride is soluble in thionyl chloride, but the resulting solution was found to be a nonconductor. The addition of various compounds such as anhydrous nickel chloride, potassium hydrogen fluoride, sodium hydrogen sulfite, or sodium acetate failed to give conducting solutions. In these attempts graphite electrodes were used since copper reacts with thionyl chloride.

Sulfuryl chloride.—This solvent was used in about the same way as thionyl chloride and, although the solution containing tantalum chloride had a slight conductivity, no metallic cathode deposit was obtained. After electrolysis the graphite electrodes were found to be coated with a white powder.

Phosphorus(III) chloride.—Tantalum(V) chloride dissolves readily in this solvent but the resulting solution was found to be a nonconductor. Addition of potassium chloride, potassium hydrogen fluoride or anhydrous nickel chloride failed to improve the conductivity of the solution.

Acetamide.—This compound at and above its melting point, 81 C, was found to be a good solvent for tantalum(V) chloride. The resulting solution showed good conductivity but on electrolysis, using graphite anodes and a copper cathode, a white precipitate, but no metallic plate, appeared on the cathode. The green solution which resulted when anhydrous nickel chloride was added gave, on electrolysis, a very thin metallic plate of nickel.

Ethylene diamine.—This compound reacted vigorously with tantalum(V) chloride with the formation of a flocculent precipitate. The precipitation did not appear to be complete which suggested the formation of a soluble complex of tantalum. The supernatant liquid was a good conductor, but on electrolysis no cathode deposit was obtained.

CONCLUSIONS

In all the tests, no electrodeposited tantalum or tantalum alloy was obtained. It seems reasonable to conclude that, so far as published information is concerned, tantalum has not yet been electrodeposited from aqueous solutions. The fact that electrodeposited tantalum or tantalum alloys are not commercially available at the present time indicates that either the claims made for the patented plating baths are too optimistic or that essential facts are not disclosed.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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THE ELECTRODEPOSITION OF MOLYBDENUM FROM AQUEOUS SOLUTIONS[1,2]

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ABSTRACT

Metallic molybdenum can be electrodeposited from aqueous solutions of molybdic acids containing high concentrations of salts. Formates, acetates, propionates, fluorides and phosphates of sodium, potassium, and ammonium have been used. The optimum pH range as measured with a glass electrode is 5.5 to 6.8. The current density may be varied from 0.06 to 3.3 amp/cm^2; the temperature should be held between 30 C and 55 C. Deposits have been obtained on copper, nickel, and iron cathodes; platinum or carbon may be used as the anode. Cobalt, nickel, and iron have been codeposited with molybdenum from solutions containing salts of these metals.

INTRODUCTION

The electrodeposition of molybdenum from aqueous media is complicated by a number of factors. In its most stable valence state, six, molybdenum forms acidic compounds; molybdenum may be reduced to lower valence states in which alkali-insoluble hydroxides or basic salts are formed. Molybdenum belongs to a group of metals characterized by a high discharge potential. The hydrogen overvoltage of molybdenum is low, and, therefore, hydrogen will be discharged simultaneously with molybdenum from aqueous solutions.

The electrodeposition of molybdenum has been attempted in the past by many investigators with little or no success. Fused or molten baths were used by J. G. Children (1), K. W. Kastner (2), Junot (3), G. Gin (4), T. R. Förland (5), Siemens and Halske (6), Hellmuth Hartman and Ullrich Conrad (7), and N. N. Tumanov (8).

Nonaqueous baths, such as solutions of molybdenum salts in organic solvents or in liquid ammonia, for the electrodeposition of metallic molybdenum have been investigated. In 1928, L. St.C. Bourghall described in a patent (9) the use of a liquid ammonia bath for the electrodeposition of molybdenum from its salts such as a halide, nitrate, cyanide, or thiocyanate. K. Wolf (10) reported that he was able to deposit metallic molybdenum sometimes by electrolyzing an alcoholic solution of the black dihydroxide of molybdenum. He adds, however, that hydrogen and the oxychloride, $Mo_3(OH)_2Cl_4$, are the main cathode products obtained from this bath.

[1] Manuscript received December 20, 1948. This paper prepared for delivery before the Chicago Meeting, October 12 to 15, 1949.

[2] This communication constitutes a portion of a dissertation submitted by Sister Mary Joecile Ksycki to the Faculty of the Graduate School of St. Louis University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Professor of Chemistry, Webster College, St. Louis, Missouri.

[4] Director of Research, Fansteel Metallurgical Corporation, Chicago, Illinois. Professor of Chemistry, St. Louis University, at the time this investigation was undertaken.

The aqueous baths for electrodeposition of molybdenum, as described in the literature, are of two types: (*a*) acid baths, and (*b*) alkaline baths.

With one exception, no alkaline bath has been claimed to give metallic deposits of molybdenum upon electrolysis. I. G. Farbenind (11) claims that thin layers of molybdenum, tungsten, vanadium, beryllium, bismuth, and tantalum are deposited on iron or copper base by electrolysis of strongly alkaline lyes saturated with oxide or hydroxide of the desired metal, the ground metal forming the cathode. But, Thompson and Kaye (12) observed that the only cathode products obtainable from a potassium hydroxide solution were oxides of molybdenum and molybdates.

Acidic baths containing molybdenum produced thin metallic deposits or none at all. C. G. Fink and C. H. Eldridge (13) reported that slight deposits of molybdenum can be obtained from an electrolyte containing molybdic acid and an excess of boric acid.

Wm. P. Price and O. W. Brown (14) reported that they obtained only very thin, steel gray deposits of molybdenum, under very carefully controlled conditions, from a solution prepared by the electrolytic reduction of molybdic acid anhydride dissolved in sulfuric acid (1.450 sp gr).

K. A. Paul (15) describes conditions under which metallic molybdenum deposits at a current density of 75 amp/sq in. from acid solutions.

Thin metallic deposits of molybdenum were obtained from a potassium citrate bath acidified with citric acid (16). However, the character of the plate was not satisfactory.

This work was undertaken to discover conditions which might yield bright electrodeposits of molybdenum from aqueous solutions. In making a general investigation of baths which might serve as media for the electrodeposition of molybdenum, numerous and various types of electrolytes were prepared and electrolyzed under varying condition of time of electrolysis, temperature, electrolyte, and current density. Among the electrolytes used were hydrochloric acid baths containing various quantities of ammonium and potassium chloride, glycerine, aluminum chloride, glue, ethyl acetate, trimethylamine; sulfamic acid baths containing ammonium hydroxide; oxalic acid baths with and without potassium carbonate; sulfuric acid baths containing glycerine, dextrose, alcohol, ammonium sulfate, or potassium sulfate; monochloracetic acid baths with and without ammonium chloride; citric acid baths with and without dextrose and ammonium citrate; boric acid baths; concentrated solution of calcium chloride, with and without dextrose; perchloric acid solutions; sulfanilic acid baths; alkaline baths, such as solutions of molybdic oxide in sodium carbonate and potassium carbonate, with and without addition agents such as dextrose, resorcinol, and pyrogallic acid.

In most cases, only oxides—yellow, brown, red, green, black—of molybdenum were obtained at first, but after several hours of preliminary electrolysis we observed that thin, dull metallic molybdenum did deposit on the cathode from some of the electrolytes.

However, the results of numerous preliminary experiments with acetate, formate, propionate, fluoride, and phosphate baths showed that bright metallic deposits of molybdenum can be deposited from these electrolytes provided that the anion concentration is high and the pH of the solution is controlled within definite limits.

This paper presents a general survey of conditions under which deposition

of metallic molybdenum was found to occur. Although it was impossible to complete a quantitative study of plating conditions, it is believed that these qualitative observations will be of interest.

EXPERIMENTAL PROCEDURE

Pyrex beakers, 150 ml and 250 ml capacity, served as cells; copper, iron, and nickel sheets in sizes 1 cm, 2 cm, and 3 cm, wide by 7 cm as cathode material; and platinum foils, 3.75 cm^2, 10 cm^2, and 40 cm^2 in area, or ashless projector carbons as anodes. The cathode strips were cleaned with steel wool, washed, dried, and weighed. After electrolysis, the cathode was immediately washed clean of electrolyte, dried, and weighed.

A direct current generator with a variable voltage control was the source of current; amperages and voltages were measured in the conventional manner. The current through the cell was controlled by a lampbank resistance unit. The cathodes were introduced into the electrolyte and removed with the circuit closed. For temperature control, the cells were heated on a water bath or cooled in a trough of cold water. A glass electrode unit, Leeds and Northrup, No. 7661-A 1 Assembly, was employed to measure the pH of the bath. "Analytical quality" reagents were used. The molybdenum compounds were ammonium molybdate, "molybdic acid, 85%," and molybdic anhydride prepared by ignition of ammonium molybdate.

In preparing the baths for electrolysis some were heated until all of the components went into solution, but most of the electrolytes contained an excess of undissolved molybdic acid.

Studies were made of the effect of various factors which influence the character of the electrode deposit. The composition of the bath—the concentration of molybdic acid; the concentration of ammonium, sodium, and potassium acetate; formate, propionate, fluorides, and phosphates; and the concentration of free acid;—was varied until the proper combination was found which gave bright metallic molybdenum plates upon electrolysis of the solution. The pH of the solution was measured with a glass electrode before and after a "run" in order to determine the rate of change in pH during electrolysis, and to determine the pH range within which bright metallic molybdenum could be deposited. The effects of current density, temperature, and time of deposition on the character of the deposit, type of metal used as cathode, and the time of deposition on current efficiency were observed.

Qualitative and quantitative tests for molybdenum were made on the plates obtained from the various baths. For qualitative analysis, the thiocyanate test, as outlined by Noyes and Bray (17), was used.

The method used for quantitative analysis of some of the plates was essentially that of W. W. Clarke (18). The weight of each deposit as determined by this method was compared to that obtained by direct weighing of the plates.

EXPERIMENTAL RESULTS

Acetate electrolytes

Bright metallic deposits of molybdenum metal were obtained from molybdic acid solutions highly concentrated with the acetate ion.

The ammonium acetate baths

Conditions under which metallic deposits of molybdenum were obtained from these baths are summarized in Table I. Best results were obtained under the following conditions:

1. Composition of the bath: 1 to 20 grams of molybdic acid (85%), 100 ml ammonium hydroxide (28%), and 95 to 108 ml acetic acid (glacial).
2. Temperature: 30 to 55 C.
3. Cathode current density: 0.5 to 3.3 amp/cm².
4. pH: 5.7 to 6.8.
5. Voltage drop: 13 to 18 v.
6. Anode: platinum or carbon.
7. Cathode: copper, nickel, or iron.

TABLE I. *Acetate baths*

A: Conditions under which bright metallic deposits of molybdenum covered the cathode.

B: Range within which metallic molybdenum deposits were obtained.

Composition of Bath		pH	Temp C	C.D.*	Time of deposition	Pre. Electrolysis	Wt of deposits	C.E.†
				amp/cm²	min	amp-hr	mg/8 cm²	%
5 g molybdate								
25 ml NH_4OH	A:	6.1	30–60	1.0	5	1		
21 ml CH_3COOH	B:		30–60	1.0	2–5			
5 g molybdate								
25 ml NH_4OH	A:	5.8	40–70	2.8	2	0		
28 ml CH_3COOH	B:	5.8–5.9	35–73	0.2–2.8	2–5			
5 g molybdate								
25 ml NH_4OH								
33 ml CH_3COOH	A:	5.2	75–85	1.1	5	1.3		
20 ml H_2O	B:		40–85	0.44–1.1	2–10			
20 g acid molyb.								
100 ml NH_4OH	A:	6.0	40–48	0.53	45	10	18.8	1
112 ml CH_3COOH	B:	5.8–6.8	40–48	0.53	1–45			
20 g acid molyb.								
100 ml NH_4OH	A:	6.0	40–55	0.67	2	9.6	1.7	1.6
105 ml CH_3COOH	B:		40–55	0.20–1.0	2			
1 g acid molyb.								
100 ml NH_4OH	A:	6.0	50–65	0.63–3.3	2	0	1–5.6	0.8–1.1
105 ml CH_3COOH	B:		30–65	0.50–3.3	1–5		0.5–5.6	1.3–0.8
1 g acid molyb.								
100 ml NH_4OH	A:	6.0	30–50	0.5	10–65	1.2	2.7–12	0.7–0.5
108 ml CH_3COOH	B:	6.0	30–50	0.5	1–65		0.5–12	1.3–0.5

* Current density.

† Current efficiency.

The experimental findings which lead to the establishment of conditions as indicated may be summarized.

1. One gram of the molybdic acid will saturate the bath; the excess may act as a reserve. When 80 ml of acetic acid are used, a black oxide is formed; between 80 and 95 ml, a mixture of blue and brown oxides is formed. When more than 108 ml are used, no metal is deposited.
2. Above 55 C a black oxide deposit tends to form. It was found that temperature and current density are interdependent factors; at higher temperatures good deposits may be obtained at higher current densities.
3. Below 0.5 amp/cm^2 very little metal is deposited. When the current density is too high, oxides are formed.
4. In too acid solutions no metal is deposited; in too alkaline solutions oxides are formed.
5. The high voltage drop is related to the high current density.
6. No noticeable differences were observed when carbon or platinum anodes were used.
7. Similar deposits were obtained on copper, nickel, and iron cathodes.

A series of experiments was conducted to observe whether potassium and sodium ions can be substituted for all or part of the ammonium ions in the previously described bath and to determine optimum conditions for deposition.

Two baths may be cited as examples of those yielding bright metallic deposits.

Potassium acetate bath

1. Composition: 5 g molybdic acid (85%), 100 g potassium acetate, 50 ml acetic acid (glacial) 130 ml water.
2. Temperature: 30–40 C.
3. Cathode current density: 0.02–0.54 amp/cm^2.
4. pH: 3.62.
5. Anode: platinum.
6. Cathode: copper.

Sodium acetate bath

1. Composition: 5 g molybdic acid (85%), 20 g sodium acetate, 36 ml acetic (glacial), 50 ml water.
2. Temperature: 40–55 C.
3. Cathode current density: 1.4 amp/cm^2.
4. pH: 3.8 to 4.2.
5. Anode: platinum.
6. Cathode: copper.

It may be noted that the pH values are lower than those used in the ammonium acetate baths. During electrolysis, the pH of the bath increases appreciably so that oxides, characteristic of too alkaline solutions, may sometimes be deposited over a layer of bright metal which had been deposited under proper conditions.

Mixed ammonium acetate-potassium acetate baths

A fourth type of acetate bath contained both ammonium and potassium acetate. Bright molybdenum can be deposited under the following conditions:

1. Composition: 5 g molybdic acid (85%); 50 g potassium acetate, 50 g ammonium acetate, 10 ml acetic acid (glacial), 50 ml water.

2. Temperature: 30–45 C.
3. Cathode current density: 0.46 amp/cm².
4. pH: 6.5.

A study of dilution effects showed that the addition of 10 ml of water to the bath as constituted had no effect on the nature of the deposit. An addition of 20 ml caused the formation of oxides on the back of the cathode where the current density was lower, while the deposit on the front was bright metal. Another 20 ml (50 ml total) formed a bath from which metal was deposited only on the edges of the cathode, oxides being formed on the back and the central area of the front. Addition of a total of 70 ml of water gave an electrolyte which yielded only black, adherent oxides. After the addition of 20 ml of acetic acid, bright metallic deposits could again be obtained.

If the solution is boiled for five minutes, 200 mg of molybdic acid (85%) will dissolve in a bath having the following composition:

50 grams of potassium acetate
50 grams of ammonium acetate
50 ml of water

Bright metallic deposits were obtained from this electrolyte at a temperature of 35 C and a current density ranging from 0.06 to 0.33 amp/cm². The pH of the bath was 6.6. During the first minute of electrolysis at a current density of 0.18 amp/cm², brown and blue oxides covered the copper cathode; during a two minute interval, the blue oxides were covered with metallic molybdenum; a ten-minute deposit was very bright and covered the cathode well. At a current density of 0.065 to 0.08 amp/cm² a metallic deposit covered an area of about 8 cm² in 105 minutes. After this long run, the solution was red but clear, and continued to give good results without reconditioning in any way. Finally, the color changed from red to almost colorless, indicating that the molybdenum was completely removed from the bath by electrolysis.

Formate electrolytes

Bright metallic deposits of molybdenum were also obtained from molybdic acid solutions containing a high concentration of formate ions. Best results were obtained under the following conditions:

1. Composition: 1 g molybdic acid (85%), 50 g potassium formate, 50 g ammonium formate, 50 ml water.
2. Temperature: 30–40 C.
3. Cathode current density: 0.6 amp/cm².
4. pH: 7.8.

When the pH of the bath was lowered to 5.5 by the addition of formic acid, a higher current density was required for the deposition of metallic molybdenum. It was observed that when the current density was decreased to 0.15 amp/cm² black oxides of molybdenum deposited on the cathode.

Propionate bath

Metallic deposits were obtained under the following conditions:

1. Composition: 5 g molybdic anhydride, 74 ml propionic acid, 32 g ammonium carbonate, 19 g potassium hydroxide, 28 ml water.
2. Temperature: 30–40 C.

3. Cathode current density: 0.15–0.4 amp/cm².
4. pH: 6.8.

Fluoride baths

It is possible to deposit smooth bright adherent deposits of molybdenum from baths in which the fluoride ion is used instead of the aliphatic acid ions as previously described: A typical bath and its operating conditions are:

1. Composition: 5 g molybdic anhydride; 100 g potassium fluoride dihydrate; 10 ml hydrofluoric acid (48%); 70 ml water.
2. Temperature: 30–50 C.
3. Cathode current density: 0.2 to 2.0 amp/cm².
4. pH: 5 (determined with Bogen's universal indicator).

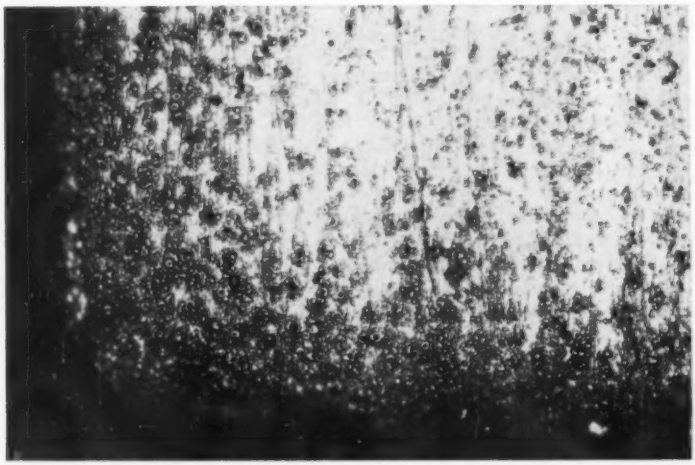

FIG. 1. Crater formation along edges of plate of average thickness 0.0015 mm (×65).

Phosphate bath

The following composition and conditions also yielded bright metallic deposits:

1. Composition: 2 g molybdic acid (85%); 5.75 g citric acid; 50 g disodium hydrogen orthophosphate hydrate; 3 ml ammonium hydroxide; 50 ml water.
2. Temperature: 30–40 C.
3. Cathode current density; 0.5 amp/cm².
4. pH: 5.4 to 8.0.

Limits of variation from the conditions as cited were not determined.

Alloy deposits

A brief preliminary study was made of the codeposition of molybdenum with iron, cobalt, and nickel. Addition of small volumes of dilute sulfate

solutions of these metals, 5 ml of solution containing 0.02 g metal per ml, to either acetate or fluoride baths yielded deposits which were shown qualitatively to contain both molybdenum and the added metal. This study was not carried further.

Microstructure of electrodeposited molybdenum

Photomicrographs[5] of various sections of the deposits of molybdenum were obtained with the aid of an "Ultrapak" microscope. Fig. 1 represents a 65 magnification of a corner of a plate obtained under the following conditions:

1. Composition: 1 g acid molybdic (85%), 100 ml ammonium hydroxide, 105 ml glacial acetic acid.
2. Temperature: 30–50 C.
3. Cathode current density: 0.5 amp/cm^2.
4. pH: 6.0.
5. Time: 65 minutes.

The metallic deposit appeared smooth, slightly dull on the edges, and covered both sides of the cathode. However, the photomicrograph of the deposit shows a multitude of tiny craters on the surface of the deposit along the edges where the current density is highest. A photomicrograph of the center of the plate (not shown in this paper) revealed very few pits.

It is not surprising to find pits in metallic deposits which have been discharged simultaneously with hydrogen gas. The number of pits decreases with a decrease in current density.

DISCUSSION

The deposits are characterized by excellent adherence to the base metal. The physical appearance of the deposits of approximately 0.001 mm thickness is that of a smooth white metal with a high luster; the thicker deposits (above 0.0015 mm) have a duller appearance, particularly around the edges of the cathode where the current density is higher. Microscopic examination of edges revealed the presence of small craters, characteristic of deposits formed simultaneously with the discharge of hydrogen gas. The adherence of small bubbles of gas blocks off deposition of the metal from the area covered by the bubble. This explains the difficulty encountered in attempts to increase the thickness of smooth metallic molybdenum deposits.

Of all the factors involved in the deposition of molybdenum, the mole ratio of anion to water appears to be the most important. The limiting ratios for the electrolytes are indicated:

$$\frac{H_2O}{\text{formate}} = 1.6 \text{ to } 2.0; \quad \frac{H_2O}{\text{acetate}} = 1.8 \text{ to } 3.5; \quad \frac{H_2O}{\text{fluoride}} = 3.6 \text{ to } 6.6$$

In the case of the propionate bath, a ratio

$$\frac{H_2O}{\text{propionate}} = 1.6$$

gave deposits, but the range was not determined. As a hypothesis, it may be suggested that the lower valent molybdenum states, formed during the

[5] Photomicrographs were taken by Philip A. Conrath, Artist in the School of Medicine, St. Louis University.

stepwise reduction from a valence of six, are more soluble in the presence of a high concentration of anions than they are in water. The molybdenum is thus prevented from precipitation as a basic salt before final reduction to metal. Dilution of the electrolyte in respect to anion prevents deposition of the metal and favors deposition of oxides even though all other conditions, such as pH and current density are kept constant.

The identity of the cathode material does not appear to be critical; similar deposits have been obtained on copper, iron, and nickel. Cathodic current efficiency was low even under the best conditions. The maximum current efficiency 2.3 per cent was obtained from an acetate bath: 5 g molybdic acid, 85%, 50 g potassium acetate, 50 g ammonium acetate, 10 ml glacial acetic acid, and 50 ml water. The current density was 0.46 amp/cm^2 and the temperature 30 C. The cathodes were plated on both sides with bright metallic molybdenum. In two minutes, 1.7 mg of metal was deposited. The maximum weight of a metallic deposit obtained in fifty minutes on a 10 cm^2 area at 4 amperes was 28 mg. The plate was approximately 0.003 mm thick.

The mechanics of deposition is open to question. The facts that large volumes of hydrogen are evolved at the comparatively high current densities and that oxides are deposited when conditions are not favorable suggest that molybdenum metal may be formed by reduction of oxides in situ by hydrogen.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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